

Computational Statistical Mechanics

Lecture notes

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Contents

1	Recall of statistical mechanics	3
1.1	Microcanonical ensemble	3
1.2	Canonical ensemble	4
1.3	Classical limit of statistical mechanics [$\hbar \rightarrow 0$]	6
2	Monte Carlo integration	10
2.1	Hard-sphere model	10
2.1.1	Hit-and-miss Monte Carlo: excluded volume	10
2.2	Complex systems (ensemble of N particles)	14
2.3	Importance sampling	15
3	Markov chains and the Metropolis algorithm	16
3.1	Markov chain	16
3.1.1	Update of the system's state	17
3.1.2	A neat example: calculation of the average depth of the Nile	20
3.2	Metropolis MC for a system of N particles	21
3.2.1	Efficiency	22
3.3	MC on lattice (e.g. Ising model)	24
4	Interaction potentials	25
4.1	Morse potential (diatomic molecule)	25
4.2	Polymers	26
4.3	Lennard-Jones	26
4.4	Soft sphere potential	27
4.5	Scaling laws of soft-sphere fluid	27
4.6	Coulomb interactions	29
4.7	Hard spheres and square well	30
4.8	Truncation, shift and smoothing of interaction potentials	30
4.8.1	Example : simulation of a polymer melt (Kremer–Grest model)	31
5	Setting up a simulation	33
5.1	Surface effects	33
5.1.1	Infinite replicas of the system	33
5.1.2	Minimum image convention	34
5.2	Initial configuration	36
5.2.1	Cubic lattice	36
5.2.2	Higher ϕ : body centred cubic (BCC)	36
5.2.3	Even higher ϕ : face centred cubic (FCC)	37
5.3	Linked cell lists	37
5.4	Nearest neighbour lists (NNL)	38

6	Measuring observables	40
6.1	Radial distribution function	40
6.1.1	Two-point density	41
6.1.2	Alternative ways of calculating 1-point and 2-point densities	42
6.1.3	$\rho^{(2)}(\vec{r}', \vec{r})$ in the homogeneous case	43
6.1.4	Average value of $g(\vec{r})$ over a volume ΔV around $\vec{r}$	43
6.1.5	Isotropic case	45
6.2	Calculation of energy from $g(r)$	46
6.3	Tail corrections	46
6.4	Calculation of pressure from $g(r)$	47
6.4.1	Tail corrections	50
6.5	Static structure factor	51
6.6	Mean squared displacement	52
7	The isothermal–isobaric (NPT) ensemble	53
7.1	Metropolis Monte Carlo in the NPT ensemble	53
7.1.1	1) Particle move	55
7.1.2	2) Volume move	55
7.2	Lennard-Jones phase diagram	56
7.2.1	Gibbs free energy	57
7.2.2	Histogram reweighting	59
7.3	Changes of the box shape (Parrinello–Rahman)	59
7.3.1	Box volume	60
7.3.2	Special cases	62
8	Orientalional moves	63
8.1	Uniaxial particles	63
8.2	Non-uniaxial particles	64
8.3	A closer look at the rotation matrix	66
8.4	Random unit vectors	67
8.5	Another possibility: quaternions	68

Chapter 1

Recall of statistical mechanics

1.1 Microcanonical ensemble

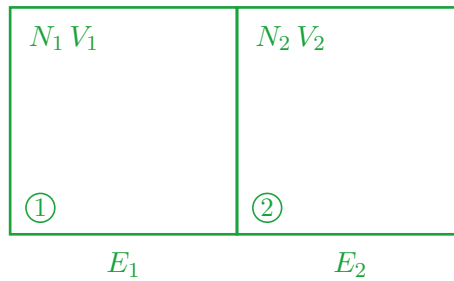


Figure 1.1: Two subsystems ① and ② exchanging energy.

HYPOTHESES

- isolated system;
- ① and ② weakly coupled;
- microscopic equiprobability.

Total energy:

$$E = E_1 + E_2 \quad \Longrightarrow \quad E_2 = E - E_1,$$

and E is conserved. Let

$$\Omega_1(E_1) = \{\# \text{ microscopic states of system } ① \text{ with energy } E_1\},$$

$$\Omega_2(E_2) = \{\# \text{ microscopic states of system } ② \text{ with energy } E_2\}.$$

The total number of microscopic states is

$$\Omega(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2).$$

Ω , Ω_1 and Ω_2 are huge, hence the use of the logarithm is convenient, i.e.

$$\ln[\Omega(E_1, E_2)] = \ln[\Omega_1(E_1)] + \ln[\Omega_2(E_2)].$$

But $E_2 = E - E_1$, so that

$$\ln[\Omega(E_1, E - E_1)] = \ln[\Omega_1(E_1)] + \ln[\Omega_2(E - E_1)].$$

Question: what is the most likely value of E_1 ?

We must enforce the condition

$$\frac{\partial \ln[\Omega(E_1, E - E_1)]}{\partial E_1} = 0,$$

i.e.

$$\left. \frac{\partial \ln[\Omega_1(E_1)]}{\partial E_1} - \frac{\partial \ln[\Omega_2(E_2)]}{\partial E_2} \right|_{E_2=E-E_1} = 0 \implies \left. \frac{\partial \ln[\Omega_1(E_1)]}{\partial E_1} \right|_{E_2=E-E_1} = \left. \frac{\partial \ln[\Omega_2(E_2)]}{\partial E_2} \right|_{E_2=E-E_1}.$$

If we define

$$\left. \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right|_{N_1, V_1} = \beta_1, \quad \left. \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right|_{N_2, V_2} = \beta_2,$$

we have the condition

$$\beta_1 = \beta_2.$$

Question: what does it mean?

$$[\beta] = \frac{1}{[E]}.$$

Define

$$S \equiv k_B \ln[\Omega(N, V, E)] = S(N, V, E)$$

and we call it entropy.

We have that

$$\frac{\partial(k_B \ln \Omega_1(E_1))}{k_B \partial E_1} = \frac{\partial(k_B \ln \Omega_2(E_2))}{k_B \partial E_2} \implies \frac{1}{k_B} \frac{\partial S_1}{\partial E_1} = \frac{1}{k_B} \frac{\partial S_2}{\partial E_2}.$$

But

$$\left[\frac{\partial S}{\partial E_1} \right] = \frac{1}{[T]},$$

hence

$$\frac{1}{k_B T_1} = \frac{1}{k_B T_2}, \quad \text{i.e.} \quad \boxed{T_1 = T_2} \quad \text{equilibrium condition!}$$

and

$$\beta_1 = \frac{1}{k_B T}, \quad \beta_2 = \frac{1}{k_B T}.$$

1.2 Canonical ensemble

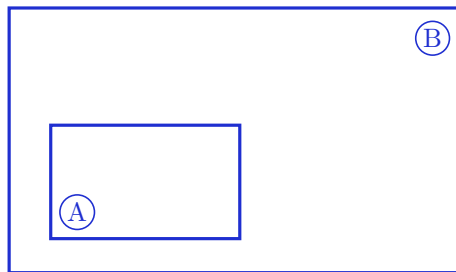


Figure 1.2: System (A) in contact with the much larger system (B).

HYPOTHESES

- the system ((A) + (B)) is isolated;

- $E_A \ll E_B$ (i.e. (B) is a thermal bath);
- (A) and (B) weakly coupled.

Let $|i\rangle$ be a quantum state of (A), and

$$P_i = \{\text{probability for (A) of being in state } |i\rangle\}.$$

Goal: calculate P_i .

Let

$$E_i = \{\text{energy of (A) being in state } |i\rangle\}, \quad E_i + E_B = E.$$

Then

$$\Omega(i, E_B) = \Omega(i, E - E_i) = \Omega_A(i) \cdot \Omega_B(E - E_i),$$

so that

$$P_i \equiv \frac{\Omega(i, E_B)}{\sum_i \Omega(i, E_B)}.$$

Again we make use of the logarithm:

$$\ln \Omega(i, E - E_i) = \ln \Omega_A(i) + \ln \Omega_B(E - E_i).$$

But $E_i \ll E$, hence

$$\ln \Omega_B(E - E_i) \simeq \ln \Omega_B(E) - E_i \underbrace{\left. \frac{\partial \ln \Omega_B}{\partial E_B} \right|_{E_B=E}}_{=\beta}.$$

Moreover

$$\Omega_A(i) = 1 \quad \implies \quad \ln \Omega_A(i) = 0,$$

thus having

$$\ln \Omega(i, E - E_i) \simeq \ln \Omega_B(E) - \beta E_i.$$

By plugging this into the definition of P_i one has

$$P_i = \frac{\cancel{\Omega_B(E)} e^{-\beta E_i}}{\sum_i \cancel{\Omega_B(E)} e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}.$$

If we define

$$Q = \sum_i e^{-\beta E_i}$$

we have

$$P_i = \frac{e^{-\beta E_i}}{Q}.$$

Q is called the **partition function**.

From Q one can calculate the internal energy U :

$$U \equiv \langle E \rangle = \frac{1}{Q} \sum_i E_i e^{-\beta E_i}.$$

But, since $Q = \sum_i e^{-\beta E_i}$,

$$\frac{\partial \ln Q}{\partial \beta} = \frac{1}{Q} \frac{\partial}{\partial \beta} \left(\sum_i e^{-\beta E_i} \right) = -\frac{1}{Q} \sum_i E_i e^{-\beta E_i} = -U,$$

hence

$$U = -\frac{\partial \ln Q}{\partial \beta}.$$

Question: is there a relation between the free energy and Q ?

From thermodynamics:

$$F = U - TS, \quad F = F(T, V).$$

Then

$$\begin{aligned} \left. \frac{\partial(F/T)}{\partial(1/T)} \right|_V &= \frac{1}{T} \frac{\partial F}{\partial(1/T)} + F = \frac{1}{T} \left. \frac{\partial F}{\partial T} \right|_V \frac{\partial T}{\partial(1/T)} + F = \frac{1}{T} \left. \frac{\partial F}{\partial T} \right|_V \frac{1}{\frac{\partial(1/T)}{\partial T}} + F \\ &= -T \left. \frac{\partial F}{\partial T} \right|_V + F. \end{aligned}$$

But

$$\left. \frac{\partial F}{\partial T} \right|_V = -S,$$

hence

$$\left. \frac{\partial(F/T)}{\partial(1/T)} \right|_V = TS + F = \mathcal{TS} + U - \mathcal{TS} = U,$$

i.e.

$$\frac{\partial(F/T)}{\partial(1/T)} = U = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial(\ln Q)}{\partial(\frac{1}{k_B T})},$$

from which it follows that

$$\frac{F}{T} = -k_B \ln Q, \quad F = -k_B T \ln Q$$

— the workhorse of statistical mechanics (with $Q = \sum_i e^{-\beta E_i}$).

1.3 Classical limit of statistical mechanics [$\hbar \rightarrow 0$]

Let $\hat{A}$ be an observable. Then

$$\underbrace{\langle \hat{A} \rangle}_{\substack{\uparrow \\ \text{statistical} \\ \text{average}}} = \frac{\sum_i \langle i | \hat{A} | i \rangle e^{-\beta E_i}}{Q} \quad P_i = \frac{e^{-\beta E_i}}{Q}$$

where

$$\hat{\mathcal{H}} |i\rangle = E_i |i\rangle \quad \longleftarrow |i\rangle \text{ eigenstates of } \hat{\mathcal{H}}.$$

Instead of eigenstates of $\hat{\mathcal{H}}$ we can use a generic complete set, i.e.

$$\langle \hat{A} \rangle = \frac{\sum_\alpha \langle \alpha | \hat{A} e^{-\beta \hat{\mathcal{H}}} | \alpha \rangle}{Q}$$

where $|\alpha\rangle$ is a complete¹ set of states, i.e.

$$\sum_\alpha |\alpha\rangle \langle \alpha| = \mathbb{I} \quad \uparrow \\ \text{identity}$$

The complete set is **arbitrary!** Non-diagonal terms are 0 $\rightarrow$ postulate (see Huang 8.7).

Let's assume further that

$$\hat{A} = \hat{A}(\hat{q}), \quad \hat{\mathcal{H}} = \hat{K}(\hat{p}) + \hat{V}(\hat{q})$$

¹Not necessarily orthonormal.

with

$$\hat{K} = \sum_i^N \frac{\hat{p}_i^2}{2m}, \quad \hat{V} = \sum_i^N \frac{k}{2} \hat{q}_i^2.$$

$$\int d^{3N}q |q\rangle\langle q| = \mathbb{I}, \quad \int d^{3N}p |p\rangle\langle p| = \mathbb{I},$$

so that

$$\langle \hat{A} \rangle = \frac{\int d^{3N}q \langle q | \hat{A} e^{-\beta \hat{\mathcal{H}}} | q \rangle}{Q}.$$

Let

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

You can easily prove that

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C} \quad (1)$$

and

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}. \quad (2)$$

From these, if $F(\hat{p})$ and $G(\hat{q})$ are smooth functions of $\hat{p}$ and $\hat{q}$ respectively, one has

$$[\hat{q}, F(\hat{p})] = i\hbar \frac{\partial F(\hat{p})}{\partial \hat{p}} \quad (3)$$

and

$$[\hat{p}, G(\hat{q})] = -i\hbar \frac{\partial G(\hat{q})}{\partial \hat{q}} \quad (4)$$

[see Sakurai, Sec. 2.2, p. 85]

We have:

$$-\beta \hat{\mathcal{H}} = -\beta \hat{K} - \beta \hat{V}.$$

The BCH formula tells us

$$e^{\hat{A}} e^{\hat{B}} = \exp \left\{ \hat{A} + \hat{B} + \frac{1}{2} [\hat{A}, \hat{B}] + \frac{1}{12} ([\hat{A}, [\hat{A}, \hat{B}]] + [\hat{B}, [\hat{B}, \hat{A}]]) + \dots \right\}$$

with $\hat{A} + \hat{B} = -\beta \hat{\mathcal{H}}$. If we set $\hat{A} = -\beta \hat{K}$ and $\hat{B} = -\beta \hat{V}$, the BCH formula yields:

$$e^{-\beta \hat{K}} e^{-\beta \hat{V}} \simeq \exp \left\{ -\beta \left(\hat{K} + \hat{V} - \frac{\beta}{2} [\hat{K}, \hat{V}] + \frac{\beta^2}{12} ([\hat{K}, [\hat{K}, \hat{V}]] + [\hat{V}, [\hat{V}, \hat{K}]] + \dots) \right) \right\}.$$

But

$$[\hat{K}, \hat{V}] = \frac{k}{4m} [\hat{p}^2, \hat{q}^2] = -\frac{k}{4m} 2i (\hat{q}\hat{p} + \hat{p}\hat{q}) \hbar = \mathcal{O}(\hbar)$$

and similarly

$$\begin{aligned} [\hat{K}, [\hat{K}, \hat{V}]] &= \mathcal{O}(\hbar^2), \\ [\hat{V}, [\hat{V}, \hat{K}]] &= \mathcal{O}(\hbar^2), \end{aligned}$$

where we made use of relations (1)–(4).

Hence in the limit $\hbar \rightarrow 0$ we can neglect $\mathcal{O}(\hbar)$ terms.

Note that $\hbar \rightarrow 0$ is equivalent to letting $\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \rightarrow 0$,

so that

$$e^{-\beta\hat{\mathcal{H}}} = e^{-\beta\hat{K}-\beta\hat{V}} \simeq e^{-\beta\hat{K}} e^{-\beta\hat{V}}.$$

Let's work out the partition function:

$$\begin{aligned} Q &= \int d^{3N}q \langle q | e^{-\beta\hat{\mathcal{H}}} | q \rangle \\ &= \int d^{3N}q \langle q | e^{-\beta\hat{K}} e^{-\beta\hat{V}} | q \rangle. \end{aligned}$$

If we insert $\int d^{3N}p |p\rangle\langle p| = \mathbb{I}$ we have

$$\begin{aligned} Q &= \int d^{3N}q d^{3N}p \langle q | e^{-\beta\hat{K}} | p \rangle \langle p | e^{-\beta\hat{V}} | q \rangle \\ &= \int d^{3N}q d^{3N}p \exp \left[-\beta \overbrace{(K(p) + V(q))}^{\text{functions of } q \text{ and } p} \right] \langle q | p \rangle \langle p | q \rangle. \end{aligned}$$

But

$$\langle q | p \rangle = \frac{1}{(2\pi\hbar)^{3N/2}} e^{i\frac{p \cdot q}{\hbar}}, \quad \langle p | q \rangle = \frac{1}{(2\pi\hbar)^{3N/2}} e^{-i\frac{q \cdot p}{\hbar}}$$

[see Sakurai, Sec. 1.7, pp. 54–56]

Hence we obtain

$$\langle q | p \rangle \langle p | q \rangle = \frac{1}{(2\pi\hbar)^{3N}},$$

thus having

$$Q = \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} \underset{\substack{\uparrow \\ \text{correct Boltzmann counting}}}{N!}} e^{-\beta\mathcal{H}(q,p)} \quad \longleftarrow \quad \mathcal{H}(q,p): \text{ function of } q \text{ and } p$$

(correct Boltzmann counting: wave functions must be either symmetric or antisymmetric).

Similarly one can treat

$$\int d^{3N}q \langle q | \hat{A} e^{-\beta\hat{\mathcal{H}}} | q \rangle$$

to have

$$= \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} A(q,p) e^{-\beta\mathcal{H}(q,p)}, \quad \mathcal{H} = K + V,$$

to finally have, in the limit $\hbar \rightarrow 0$,

$$\langle A \rangle = \frac{\int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} A e^{-\beta\mathcal{H}}}{\underbrace{\int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} e^{-\beta\mathcal{H}}}_Q}.$$

But since $A = A(q)$, as we assumed, one has

$$\boxed{\langle A \rangle = \frac{\int A(q) e^{-\beta V(q)} d^{3N}q}{Z}}$$

where Z is the configurational partition function

$$Z = \int d^{3N}q e^{-\beta V(q)}.$$

Alternative way: $\beta \rightarrow 0$ (high temperatures). Just note that

$$\begin{aligned} e^{-\beta(\hat{K}+\hat{V})} &= \mathbb{I} - \beta(\hat{K} + \hat{V}) + \mathcal{O}(\beta^2) \simeq \mathbb{I} - \beta(\hat{K} + \hat{V}) \\ &= e^{-\beta\hat{K}} e^{-\beta\hat{V}} + \mathcal{O}(\beta^2). \end{aligned}$$

Chapter 2

Monte Carlo integration

2.1 Hard-sphere model

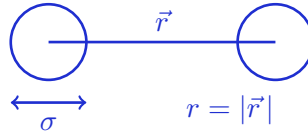


Figure 2.1: Two hard spheres of diameter σ at distance r .

$$U_{\text{HS}}(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} \quad r = |\vec{r}|.$$

$$\phi = \{\text{volume fraction}\} = \hat{v}_{\text{HS}} \frac{\overset{\text{number of particles}}{N}}{\underset{\text{volume}}{V}}$$

where

$$\hat{v}_{\text{HS}} = \frac{\pi}{6} \sigma^3;$$

$\hat{v}_{\text{HS}}N$ is the volume occupied by N spheres.

Question: why can hard spheres form a crystal?

Hard spheres are an “entropic” system since

$$F = U - TS \quad \text{but} \quad U = \frac{3}{2}k_B T N + \underbrace{U_{\text{ex}}}_{\text{excess energy}}^0,$$

hence

$$F = \frac{3}{2}k_B T N - TS = T \left(\frac{3}{2}k_B N - S \right).$$

This implies that minimizing F is equivalent to maximizing S (entropy), i.e. the number of accessible states. But

2.1.1 Hit-and-miss Monte Carlo: excluded volume

In 1D:

$$\int_a^b f(x) dx = (b-a) \underbrace{\left(\frac{1}{b-a} \int_a^b f(x) dx \right)}_{\langle f \rangle} = (b-a) \langle f \rangle.$$

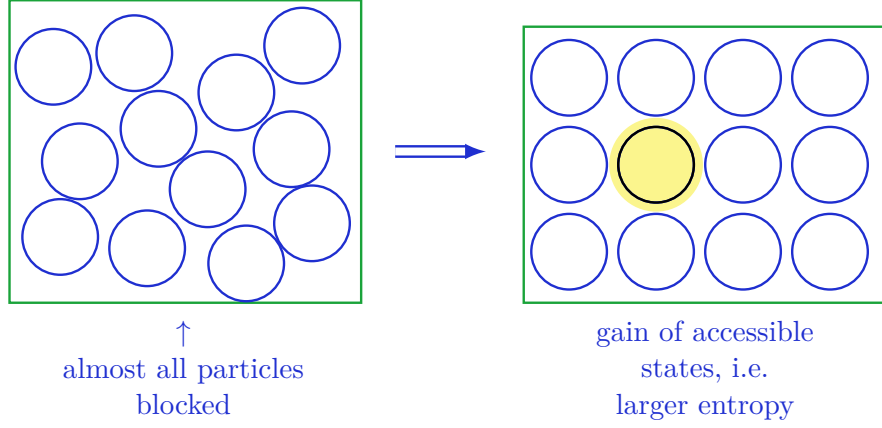


Figure 2.2: Disordered (left) vs. ordered (right) hard-sphere configurations at high density: in the crystal each particle has more room to move.

In 3 dimensions:

$$\int_V f(\vec{x}) d^3x = V \left(\frac{1}{V} \int_V f(\vec{x}) d^3x \right) = V \langle f \rangle.$$

Virial expansion:

$$\beta P = \rho - \frac{1}{2} \rho^2 \int \left(e^{-\beta U_{\text{HS}}(r)} - 1 \right) d^3r + \mathcal{O}(\rho^3).$$

Let

$$f = e^{-\beta U_{\text{HS}}(r)} - 1 \quad \longleftarrow \text{Mayer } f\text{-function};$$

then

$$\beta P = \rho - \frac{1}{2} \rho^2 \int f(r) d^3r.$$

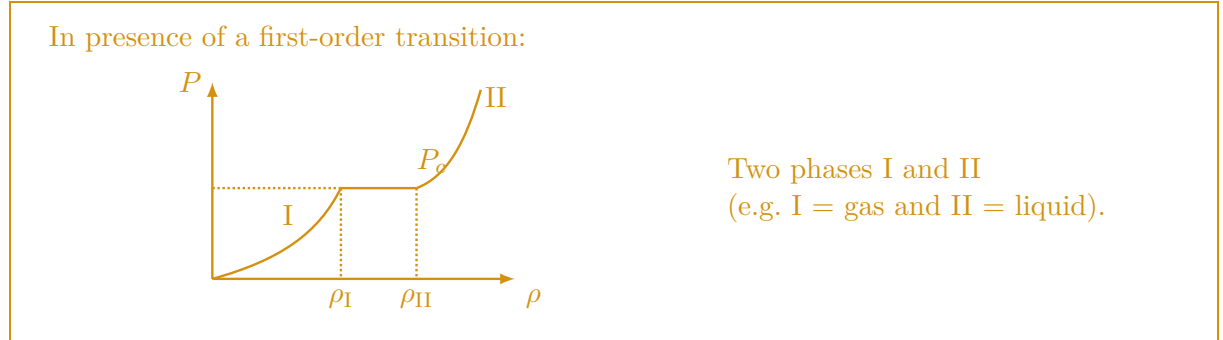


Figure 2.3: Equation of state $P(\rho)$ with a first-order transition: coexistence plateau at P_c between ρ_I and ρ_{II} .

For hard spheres

$$f = \begin{cases} -1 & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

hence

$$-\int f(r) d^3r = \{\text{volume of a sphere of radius } \sigma\} = \underbrace{\frac{4\pi}{3} \sigma^3}_{v_{\text{excl}}}.$$

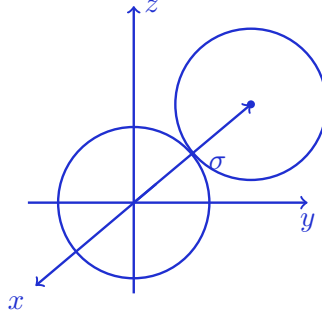


Figure 2.4: Two hard spheres in contact: centres at distance σ .

$$\beta P = \rho + \frac{\rho^2}{2} v_{\text{excl}} + \mathcal{O}(\rho^3).$$

We can calculate v_{excl} through a “hit and miss” Monte Carlo.

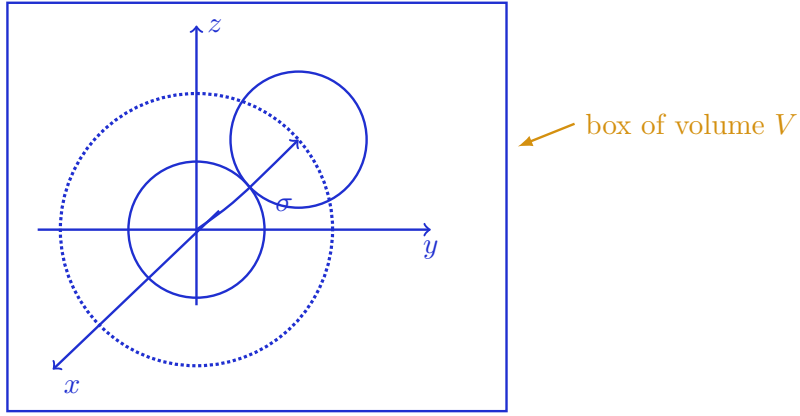


Figure 2.5: Hit-and-miss estimate of the excluded volume: a sphere is fixed at the origin; the dotted sphere of radius σ is the excluded volume.

$$v_{\text{excl}} = V \left(\frac{1}{V} \int_V \left(1 - e^{-\beta U_{\text{HS}}(r)} \right) d^3 r \right) = V \langle \tilde{f} \rangle \quad \text{where} \quad \tilde{f} = -f.$$

$\langle \tilde{f} \rangle$ can be calculated by a “hit and miss” Monte Carlo, by inserting randomly a HS given one fixed at the origin, i.e.

$$\langle \tilde{f} \rangle = \frac{1}{N} \sum_i^N \tilde{f}(\vec{r}_i) = \frac{N_{\text{ov}}}{N}$$

with

$$N = \{\text{number of insertions}\},$$

$$N_{\text{ov}} = \{\text{number of overlaps}\},$$

and note that

$$\tilde{f} = \begin{cases} 1 & r \leq \sigma \\ 0 & r > \sigma \end{cases}.$$

$$\text{Error} \propto \frac{1}{\sqrt{N}}.$$

$$v_{\text{excl}} = V \cdot \langle \tilde{f} \rangle = V \frac{N_{\text{ov}}}{N}$$

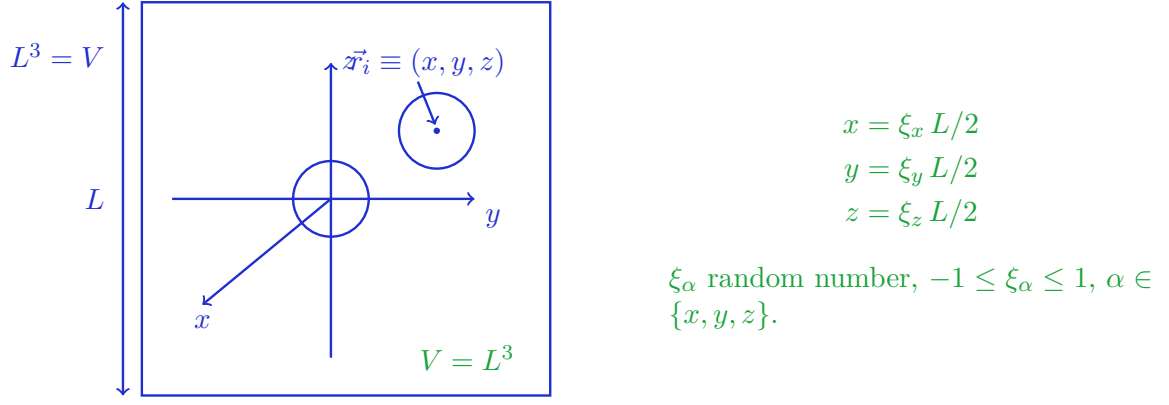


Figure 2.6: Random insertion of a hard sphere at $\vec{r}_i$ in a cubic box of side L , with another sphere fixed at the origin.

More generally, consider for example **hard ellipsoids** (HE).

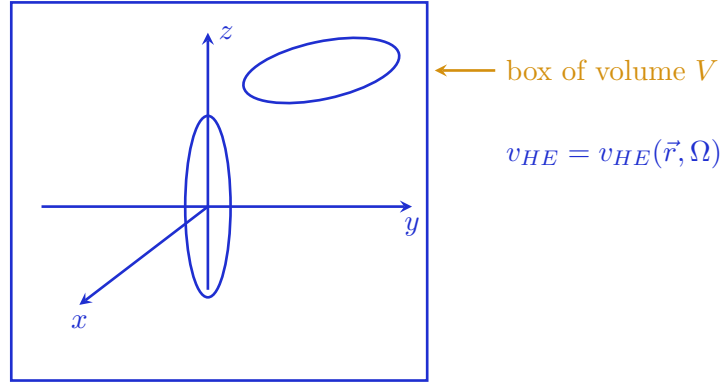


Figure 2.7: Two hard ellipsoids in a box of volume V ; their interaction depends on the relative position $\vec{r}$ and on the relative orientation Ω .

The excluded volume is

$$\begin{aligned}
 v_{\text{excl}} &= \int \left(1 - e^{-\beta v_{HE}(\vec{r}, \Omega)}\right) d^3r \frac{d\Omega}{4\pi} = V \cdot \int \left(1 - e^{-\beta v_{HE}(\vec{r}, \Omega)}\right) \frac{d^3r}{V} \frac{d\Omega}{4\pi} \\
 &= V \cdot \langle \tilde{f} \rangle,
 \end{aligned}$$

with

$$\tilde{f} = 1 - e^{-\beta v_{HE}(\vec{r}, \Omega)}, \quad \langle \tilde{f} \rangle = \int \left(1 - e^{-\beta v_{HE}(\vec{r}, \Omega)}\right) \frac{d^3r}{V} \frac{d\Omega}{4\pi}.$$

Insertion of hard ellipsoids with random positions and orientations:

$$\langle \tilde{f} \rangle = \frac{N_{ov}}{N} \quad \begin{array}{l} \leftarrow \text{number of overlaps} \\ \leftarrow \text{number of insertions} \end{array}$$

and

$$v_{\text{excl}} = V \langle \tilde{f} \rangle,$$

so that we will have a rough estimate of their equation of state

$$\beta P = \rho + \frac{\rho^2}{2} v_{\text{excl}}$$

2.2 Complex systems (ensemble of N particles)

$$A = A(q^N, p^N), \quad q^N = \{\vec{q}_1, \dots, \vec{q}_N\}, \quad p^N = \{\vec{p}_1, \dots, \vec{p}_N\},$$

$$\underbrace{\langle A \rangle}_{\text{thermodynamic average}} = \frac{1}{Q} \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} A(q^N, p^N) e^{-\beta\mathcal{H}},$$

with

$$\mathcal{H} = K + U, \quad K = \sum_i \frac{\vec{p}_i^2}{2m}, \quad U = U(\vec{q}_1, \dots, \vec{q}_N) = \frac{1}{2} \sum_{i \neq j} v(\vec{q}_i - \vec{q}_j),$$

$$Q = \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} e^{-\beta\mathcal{H}}.$$

Let's assume $A = A(q^N)$ and integrate over p^N , so that

$$\langle A \rangle = \frac{\int A(q^N) e^{-\beta U} d^{3N}q}{Z}, \quad Z = \int e^{-\beta U} d^{3N}q.$$

If we define

$$\mathcal{N}(q^N) \equiv \frac{e^{-\beta U(q^N)}}{Z}$$

one has

$$\langle A \rangle = \int_V \mathcal{N}(q^N) A(q^N) d^{3N}q.$$

If we use a standard quadrature (e.g. trapezoidal integration):

- we have $3N$ dimensions;
- assume 10 points along each direction;
- assume $N = 1000$ particles.

We will have to do

$$10^{3N} \text{ operations.}$$

If our computer can do exaflops, i.e. 10^{18} flops (very powerful!), it will take

$$\frac{10^{3 \cdot 1000}}{10^{18}} = 10^{3000-18} \simeq 10^{3000} \text{ s,}$$

to be compared with a human life,

$$3600 \times 24 \times 365 \times 100 \simeq 10^9 \text{ s.}$$

Universe? 10^{18} s ($\simeq 20$ billion years).

Yet not enough!

But MC can do the job!

$$\begin{aligned} \underbrace{\langle A \rangle}_{\text{ensemble average}} &= \int A \mathcal{N}(q^N) d^{3N}q = V^N \left(\int \frac{1}{V^N} A \mathcal{N}(q^N) d^{3N}q \right) \\ &= V^N \cdot \langle A \mathcal{N} \rangle_V, \end{aligned}$$

where $\langle A \mathcal{N} \rangle_V$ is the average of $A \mathcal{N}$ when we generate randomly points inside volume V .

In principle it is OK, but it is inefficient, since it is very likely that

$$\mathcal{N}(q^N) \simeq 0 \quad \text{if } q^N \text{ is random.}$$

Need of some improvement!

2.3 Importance sampling

1D case.

$$\overbrace{\int_a^b f(x) dx}^I = \overbrace{\int \left(\frac{f(x)}{w(x)} \right) w(x) dx}^{\langle f/w \rangle_w}, \quad \text{where } \int_a^b w dx = 1.$$

Let

$$u = u(x), \quad u(x) = \int_a^x w(x') dx' \implies du = w dx, \quad u(b) = 1, \quad u(a) = 0,$$

so that

$$I = \int_0^1 \frac{f(x(u))}{w(x(u))} \underbrace{du}_{\text{uniform distribution}} = \boxed{\left\langle \frac{f}{w} \right\rangle_w}$$

and

$$I = \frac{1}{L} \sum_{i=1}^L \frac{f(x(u_i))}{w(x(u_i))}, \quad L \text{ is the number of random points generated.}$$

If

$$g_i \equiv \frac{1}{L} \frac{f_i}{w_i}, \quad \text{where } f_i = f(x(u_i)), \quad w_i = w(x(u_i)),$$

then

$$\sigma^2(I) = \sigma^2\left(\sum_{i=1}^L g_i\right) = L \sigma^2(g_i) = L \frac{1}{L^2} \sigma^2\left(\frac{f}{w}\right),$$

i.e.

$$\sigma(I) = \frac{1}{\sqrt{L}} \sigma\left(\frac{f}{w}\right).$$

If $\frac{f}{w} \simeq \text{constant}$, then $\sigma\left(\frac{f}{w}\right) \simeq 0$.

Let's apply this technique to statistical averages, with $w = w(q_1, \dots, q_N)$:

$$\underbrace{\langle A \rangle}_{\text{statistical average}} = \int A(q^N) \frac{e^{-\beta U(q^N)}}{Z} d^{3N}q = \left\langle \overbrace{\frac{A\mathcal{N}}{w}}^f \right\rangle_w.$$

A wise choice is $w = \mathcal{N}(q^N)$, hence

$$\langle A \rangle = \left\langle \frac{A\mathcal{N}}{\mathcal{N}} \right\rangle_{\mathcal{N}} = \frac{1}{L} \sum_{i=1}^L \underbrace{A(\vec{q}_1^i, \dots, \vec{q}_N^i)}_{\text{unweighted average!}}.$$

Now we need to find a strategy to generate points according to the distribution $\mathcal{N}$, since

$$\mathcal{N} = \frac{e^{-\beta U}}{Z},$$

but Z is an integral and we can't calculate it efficiently.

Chapter 3

Markov chains and the Metropolis algorithm

3.1 Markov chain

Set of stochastic variables

$$X_t \in \{\text{finite set of possible values}\}.$$

- 1) $X_t = (\vec{q}_1, \dots, \vec{q}_N)$: set of coordinates that on a PC can assume values from a finite set;
- 2) $P(X_{t+1} = Y_{t+1} | X_t = Y_t)$, $Y_t = \text{state of the system (e.g. positions of all particles)}$;
- 3) the chain is ergodic.

Note that:

$$P(X_{t+1} = Y_n | X_t = Y_o) = \Pi_{on}$$

transition probability to go from the old state (o) to the new state (n).

Consider M systems which we are simulating in parallel:

$$Y_t = (\vec{x}_1^{(t)}, \dots, \vec{x}_N^{(t)}) \quad \leftarrow \text{positions of } N \text{ particles (state of the system).}$$

Note that they constitute a finite set, hence we can use an index k to identify them.

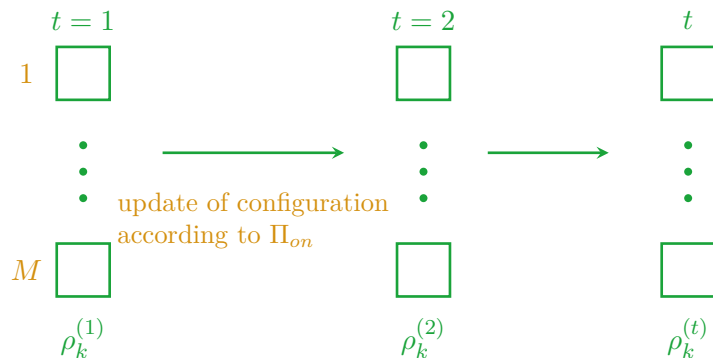


Figure 3.1: M copies of the system evolving in parallel; at each step every configuration is updated according to Π_{on} .

$\rho_k^{(t)}$ is the probability of having state k .
At $t = 1$ we will be generally “out of equilibrium”.

But if the Markov chain is ergodic

$\lim_{t \rightarrow +\infty} \rho_i^{(t)} = \rho_i$: the system “equilibrates” and tends to the **equilibrium distribution** ρ_i .

In other words, when $\rho_i^{(t)} = \rho_i$ we can say that the system is equilibrated.

Note that the transition matrix is the same for all systems and we update the system’s state as discussed in the following.

3.1.1 Update of the system’s state

Consider a system in state i . To update its state:

$$\Pi_{\text{transition matrix}} = \begin{pmatrix} \vdots \\ \Pi_{i0} \cdots \Pi_{ik} \cdots \Pi_{iN_s} \\ \vdots \end{pmatrix} \leftarrow i\text{-th row},$$

where Π_{ik} is the probability to go from state i to state k , and

$N_s = \{\text{total number of possible states}\}$.

Note that $\sum_k \Pi_{ik} = 1$.

Generate a uniform random number $\xi \in [0, 1]$:

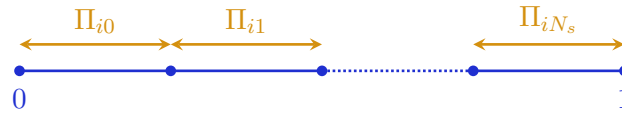


Figure 3.2: The interval $[0, 1]$ partitioned into segments of length $\Pi_{i0}, \Pi_{i1}, \dots, \Pi_{iN_s}$.

$$\begin{aligned} \text{if } \xi < \Pi_{i0} & \quad \text{then } i \rightarrow 0, \\ \text{if } \Pi_{i0} < \xi < \Pi_{i0} + \Pi_{i1} & \quad \text{then } i \rightarrow 1, \\ \vdots & \end{aligned}$$

We can view “equilibration” from a different perspective. Let’s consider the excess energy due to particle interactions:

$$U = \{\text{internal energy}\} = K + U_{\text{ex}},$$

where K is the kinetic energy and, if $\mathcal{V} = \mathcal{V}(\vec{x}_1, \dots, \vec{x}_N)$ is the potential energy of the system,

$$U_{\text{ex}} = \langle \mathcal{V}(\vec{x}_1, \dots, \vec{x}_N) \rangle.$$

Let’s consider again the M systems evolving (running) in parallel:

$$\rho_n^{(t)} \cdot M = \{\# \text{ of systems in state } n\}.$$

$\rho_n^{(t+1)}$ and $\rho_n^{(t)}$ can be related through Π_{kn} . Indeed:

$$\rho_n^{(t+1)} M = \underbrace{\rho_n^{(t)} M}_{\# \text{ of systems in state } n} + \underbrace{\sum_{k \neq n} \Pi_{kn} \rho_k^{(t)} M}_{\# \text{ systems going to state } n} - \underbrace{\sum_{k \neq n} \Pi_{nk} \rho_n^{(t)} M}_{\# \text{ systems leaving state } n \text{ (note the minus)}}.$$

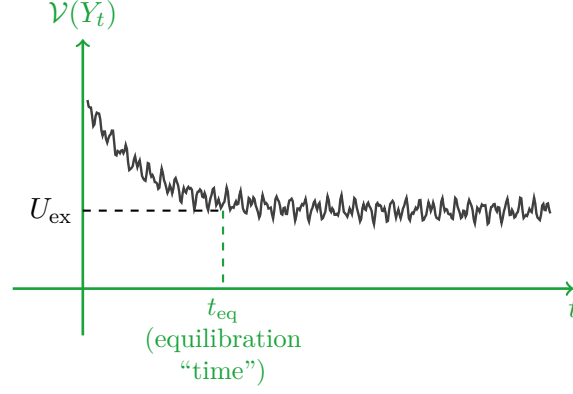


Figure 3.3: Potential energy along the Markov chain: after the equilibration “time” t_{eq} it fluctuates around U_{ex} .

But at equilibrium $\rho_n^{(t+1)} = \rho_n^{(t)} = \rho_n$, hence

$$\rho_n^{(t+1)} = \rho_n^{(t)} + \sum_{k \neq n} \Pi_{kn} \rho_k - \sum_{k \neq n} \Pi_{nk} \rho_n,$$

thus having

$$\begin{aligned} \sum_{k \neq n} \Pi_{kn} \rho_k - \sum_{k \neq n} \Pi_{nk} \rho_n &= 0, \\ \sum_{k \neq n} \Pi_{kn} \rho_k + \Pi_{nn} \rho_n &= \sum_{k \neq n} \Pi_{nk} \rho_n + \Pi_{nn} \rho_n, \\ \sum_k \Pi_{kn} \rho_k &= \sum_k \Pi_{nk} \rho_n. \end{aligned}$$

But $\sum_k \Pi_{nk} = 1$, hence

$$\sum_k \rho_k \Pi_{kn} = \rho_n,$$

which can be written in matrix form as follows:

$$\vec{\rho} \mathbf{\Pi} = \vec{\rho} \tag{1}$$

where $\vec{\rho} = (\rho_1, \dots, \rho_k, \dots)$ and $\mathbf{\Pi}$ is a matrix whose elements are $(\mathbf{\Pi})_{nk} = \Pi_{nk}$.

For an ergodic Markov chain with a finite space of states, if we consider $\vec{\rho} \mathbf{\Pi} = \lambda \vec{\rho}$, there exists a unique $\vec{\rho}$ such that $\lambda = 1$; $\mathbf{\Pi}$ is not guaranteed to be diagonalizable, and the other eigenvalues λ_k are such that $|\lambda_k| < 1$ (they can be obtained by Jordan decomposition).

Eq. (1) is called the **balance condition** and it states that the vector $\vec{\rho}$ is an eigenvector of the matrix $\mathbf{\Pi}$ with eigenvalue 1.

Eq. (1) tells us that the number of systems undergoing a transition to state n is equal to the number of systems leaving state n .

We can impose a stronger condition. Since

$$\sum_k \Pi_{kn} \rho_k = \sum_k \Pi_{nk} \rho_n,$$

that is

$$\sum_k \boxed{\Pi_{kn} \rho_k - \Pi_{nk} \rho_n} = 0,$$

which is satisfied if we require

$$\Pi_{kn} \rho_k = \Pi_{nk} \rho_n, \quad (2)$$

which is called the “detailed balance condition”.

In this case Π is diagonalizable with real eigenvalues.

This condition states that the number of systems going from state k to state n has to be equal to the number of systems going from state n to state k .

In the following $k \rightarrow o$, so that Eq. (2) becomes

$$\rho_o \Pi_{on} = \rho_n \Pi_{no} \quad (3)$$

so that we can think that o stands for “old” and n for “new”.

According to this condition we can impose the equilibrium distribution reached by the system by providing a transition probability which enforces Eq. (3), given a certain probability distribution ρ_k .

Let’s find out a way to provide Π_{on} (Monte Carlo Metropolis):

$$\Pi_{on} = \underbrace{\alpha(o \rightarrow n)}_{\text{trial move}} \underbrace{\text{acc}(o \rightarrow n)}_{\text{acceptance probability}}.$$

$\alpha(o \rightarrow n)$: update the system’s state (i.e. the particle positions) randomly, and we require

I) $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$, i.e. that it is symmetric (even if it is not necessary, as we shall see when we discuss **biased Monte Carlo**);

II) $\text{acc}(o \rightarrow n) = \min\left\{1, \frac{\rho_n}{\rho_o}\right\}$.

Note: if $\rho = \frac{e^{-\beta V}}{Z}$ then

$$\frac{\rho_n}{\rho_o} = e^{-\beta(V_n - V_o)} = e^{-\beta \Delta V},$$

where ΔV is the variation of potential energy after the trial move.

By enforcing I) and II) the detailed balance condition is fulfilled; indeed:

Case I. Consider a move such that $\rho_n < \rho_o$, then

$$\begin{aligned} \rho_o \Pi_{on} &= \rho_n \Pi_{no} \\ \rho_o \cancel{\alpha(o \rightarrow n)} \text{acc}(o \rightarrow n) &= \rho_n \cancel{\alpha(n \rightarrow o)} \text{acc}(n \rightarrow o) \\ \rho_o \underbrace{\min\left(1, \frac{\rho_n}{\rho_o}\right)}_{= \rho_n / \rho_o} &= \rho_n \underbrace{\min\left(1, \frac{\rho_o}{\rho_n}\right)}_{= 1} \\ \cancel{\rho_o} \frac{\rho_n}{\cancel{\rho_o}} &= \rho_n \implies \rho_n = \rho_n. \end{aligned}$$

Similarly one can proceed by assuming $\frac{\rho_n}{\rho_o} > 1$.

Case II. $\rho_n > \rho_o$:

$$\begin{aligned} \rho_o \underbrace{\min\left(1, \frac{\rho_n}{\rho_o}\right)}_{= 1} &= \rho_n \underbrace{\min\left(1, \frac{\rho_o}{\rho_n}\right)}_{= \rho_o / \rho_n} \\ \rho_o = \cancel{\rho_n} \frac{\rho_o}{\cancel{\rho_n}} &\implies \rho_o = \rho_o. \end{aligned}$$

3.1.2 A neat example: calculation of the average depth of the Nile

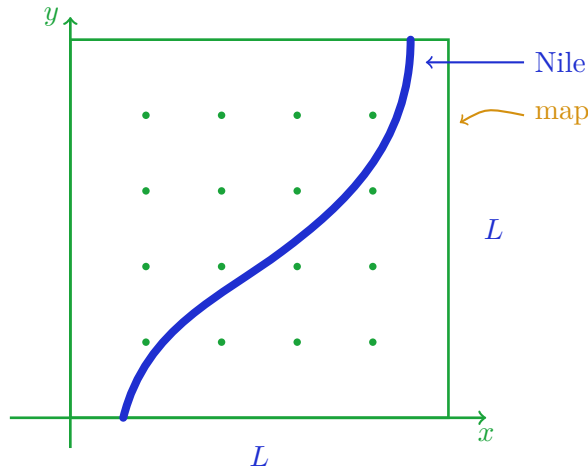


Figure 3.4: Map of side L containing the Nile.

Some definitions:

$$A = L^2 = \{\text{map area}\},$$

$$\Theta(x, y) = \begin{cases} 1 & \text{if } (x, y) \in \text{Nile}, \\ 0 & \text{otherwise,} \end{cases}$$

$$d(x, y) = \{\text{depth of terrain at } (x, y)\}$$

(note that $d(x, y)$ can be $\neq 0$ also outside the Nile).

Hence

$$S = \int_A \Theta(x, y) dx dy = \{\text{area of the Nile}\}$$

and

$$\langle d(x, y) \rangle = \int_A \frac{d(x, y) \Theta(x, y)}{S} dx dy.$$

We can calculate this integral through a standard quadrature procedure (e.g. the rectangle method) ... or we can use a Metropolis MC: $\frac{\Theta(x, y)}{S}$ is a probability distribution, indeed

$$\int_A \frac{\Theta(x, y)}{S} dx dy = 1,$$

where S is the analogue of the partition function, and $d(x, y)$ is an observable, so that

$$\int_A d(x, y) \frac{\Theta(x, y)}{S} dx dy$$

can be viewed as an ensemble average and we can employ a Metropolis MC.

Each trial move consists in randomly updating the position of the current point (i.e. the location on the map) (x_o, y_o) to a new point (x_n, y_n) and rejecting this trial move if $(x_o, y_o) \in \text{Nile}$ and $(x_n, y_n) \notin \text{Nile}$. We will end up with a random walk as follows:

[Note that “hit and miss” would be inefficient: it is very unlikely to hit the Nile.]

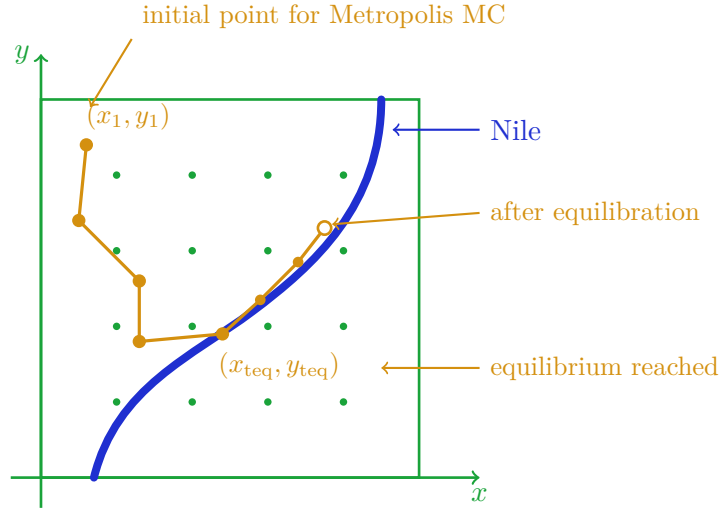


Figure 3.5: Metropolis random walk on the map: the walker starts at (x_1, y_1) , reaches the Nile at time t_{eq} and afterwards never leaves it.

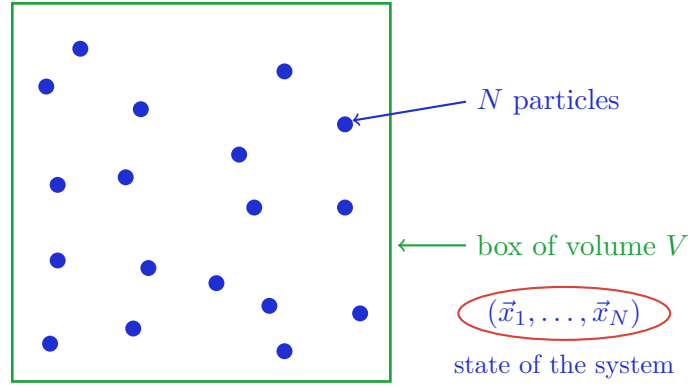


Figure 3.6: N particles in a box of volume V ; the state of the system is the set of positions $(\vec{x}_1, \dots, \vec{x}_N)$.

3.2 Metropolis MC for a system of N particles

I) Trial move $\alpha(o \rightarrow n)$. Choose randomly a particle and displace it by

$$\Delta \vec{r} = (\Delta x, \Delta y, \Delta z) \quad \boxed{1 \text{ MC step} \equiv N \text{ trial moves}}$$

where

$$\Delta x = \xi_x \delta, \quad \Delta y = \xi_y \delta, \quad \Delta z = \xi_z \delta,$$

and ξ_α are random variables such that $-1 < \xi_\alpha < 1$, with $\alpha \in \{x, y, z\}$.

II) Acceptance $\text{acc}(o \rightarrow n)$.

$$\text{acc}(o \rightarrow n) = \min \left\{ 1, \frac{e^{-\beta U_n}}{e^{-\beta U_o}} \right\} = \min \{ 1, e^{-\beta \Delta U} \}.$$

Hence if $\Delta U < 0 \implies$ **accepted**; **otherwise** draw a random variable ξ , $0 \leq \xi < 1$:

$$\text{if } \begin{cases} \xi \leq e^{-\beta \Delta U} & \text{accepted,} \\ \xi > e^{-\beta \Delta U} & \text{rejected.} \end{cases}$$

3.2.1 Efficiency

$$\eta = \{\text{efficiency}\} \equiv \frac{\overbrace{\sum_{k=1}^L \delta r_k^2}^{\text{sum over single-particle moves } (\delta r_k = 0 \text{ if rejected})}}{\tau} = \frac{\Delta r^2}{\tau}$$

Δr^2 quantifies the “total displacement”, i.e. how much the initial configuration changed, and

$$\tau = \{\text{computing time for carrying out } L \text{ trial moves}\} = \underbrace{t_1}_{\substack{\text{time needed to move one particle} \\ \text{(i.e. to calculate } \Delta U)}} L.$$

- I) If $\delta \rightarrow 0$, $\Delta r^2 \rightarrow 0$ but $\tau = t_1 \cdot L$ does not $\Rightarrow \eta \rightarrow 0$.
- II) If δ is large (e.g. larger than the particle size): with δ large it is very likely to have an overlap, so that the energy is large and the move is rejected; hence $\Delta r^2 \rightarrow 0$ but again τ is finite $\Rightarrow \eta \rightarrow 0$.

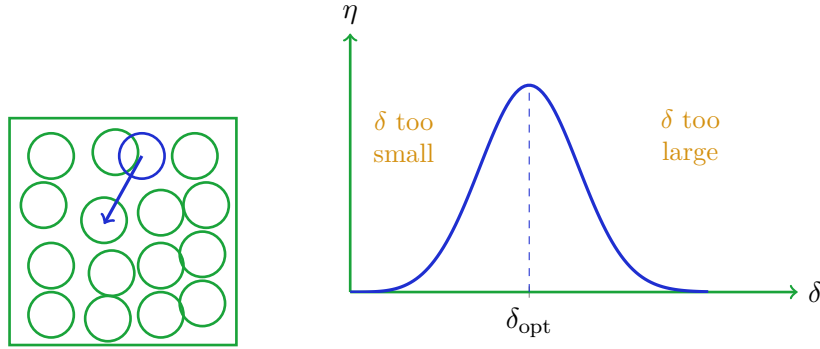


Figure 3.7: Left: with large δ a displaced particle (blue) very likely overlaps with the others. Right: efficiency η as a function of δ , with a maximum at the optimal value δ_{opt} .

Let

$$R = \{\text{acceptance rate of trial moves}\} = \frac{\{\# \text{ accepted trial moves}\}}{\{\# \text{ trial moves}\}}.$$

If

$$0.3 < R < 0.5 \quad \Rightarrow \quad \delta \approx \delta_{\text{opt}} \quad (\text{empirical rule}).$$

Question: what R do we have if we move N particles at a time?

Consider again M identical systems being simulated in the NVT ensemble (canonical ensemble). After a trial move of 1 particle (i), with $\alpha = x, y, z$:

$$\langle \Delta U \rangle = \left\langle \sum_{\alpha} \frac{\partial U}{\partial r_i^{\alpha}} \delta r_i^{\alpha} + \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 U}{\partial r_i^{\alpha} \partial r_i^{\beta}} \delta r_i^{\alpha} \delta r_i^{\beta} \right\rangle = \dots$$

where $\langle \dots \rangle$ is over all M systems:

$$\dots = \underbrace{\left\langle \sum_{\alpha} \frac{\partial U}{\partial r_i^{\alpha}} \right\rangle}_{\text{average over } M \text{ runs}} \overbrace{\delta r_i^{\alpha}}^{\text{average over trial moves}} + \left\langle \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 U}{\partial r_i^{\alpha} \partial r_i^{\beta}} \right\rangle \overline{\delta r_i^{\alpha} \delta r_i^{\beta}}.$$

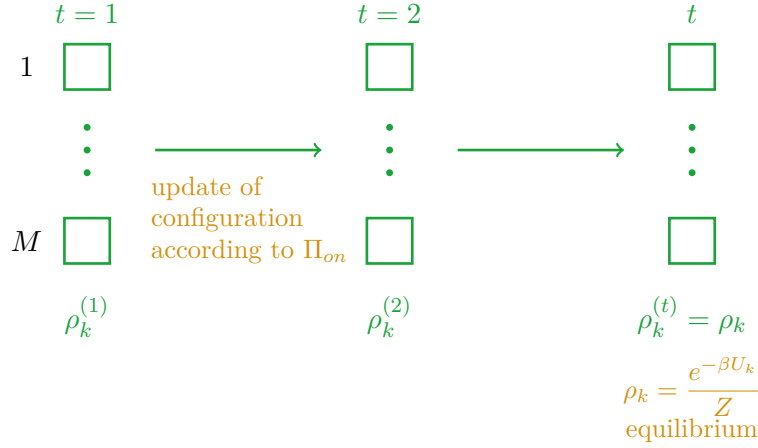


Figure 3.8: M identical systems evolving in (MC) time; at equilibrium the distribution of states over the M systems is $\rho_k = e^{-\beta U_k}/Z$.

We split the average since the average over trial moves ($\bar{x}$) is independent of the average over the M systems ($\langle x \rangle$).

But

$$\overline{\delta r_i^\alpha} = 0 \quad \text{and} \quad \overline{\delta r_i^\alpha \delta r_i^\beta} = 0 \quad \text{if } \alpha \neq \beta,$$

and

$$\overline{(\delta r_i^x)^2} = \overline{(\delta r_i^y)^2} = \overline{(\delta r_i^z)^2} = \overline{\delta r^2}.$$

Moreover

$$\left\langle \frac{1}{2} \sum_{\alpha} \frac{\partial^2 U}{\partial r_i^\alpha \partial r_i^\alpha} \right\rangle \equiv f(U),$$

hence we are left with

$$\langle \Delta U \rangle = f(U) \overline{\delta r^2}.$$

A move is likely accepted if $\langle \Delta U \rangle \simeq k_B T$, thus having

$$f(U) \overline{\delta r^2} = k_B T \implies \overline{\delta r^2} = \frac{k_B T}{f(U)},$$

that is, if we move 1 particle at a time, L times:

$$\eta_1 = \frac{L \overline{\delta r^2}}{L t_1} = \frac{\overline{\delta r^2}}{t_1} = \frac{k_B T}{t_1 f(U)}.$$

If we attempt to move N particles at a time

$$\langle \Delta U \rangle = f(U) \overline{\delta r^2} N,$$

since we have contributions from N particles (not just the i -th particle as before). Hence

$$\overline{\delta r^2} = \boxed{\frac{k_B T}{N f(U)}} \rightarrow \text{average displacement of a single particle after a trial move.}$$

Note that in

$$\eta = \frac{\sum_k \delta r_k^2}{\tau}$$

$\sum_k \delta r_k^2$ is now a sum over all particle displacements after L trial moves, i.e.

$$\sum_k \delta r_k^2 = L \cdot N \cdot \overline{\delta r^2}.$$

Hence the efficiency η_N of moving simultaneously N particles after L trial moves is

$$\eta_N = \frac{\overline{\delta r^2} L N}{t_1 L N} = \frac{k_B T}{N t_1 f(U)} = \frac{1}{N} \underbrace{\frac{k_B T}{t_1 f(U)}}_{=\eta_1},$$

so that

$$\eta_N = \frac{\eta_1}{N},$$

i.e. η_N is N times smaller than η_1 !

3.3 MC on lattice (e.g. Ising model)

Each MC step consists in updating the state of a lattice site.

Chapter 4

Interaction potentials

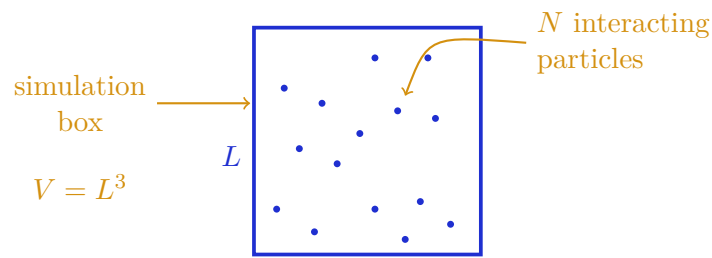


Figure 4.1: Simulation box of volume $V = L^3$ containing N interacting particles.

$$U = \frac{1}{2} \sum_{i \neq j} \underbrace{U_2(\vec{r}_i, \vec{r}_j)}_{\text{2-body interactions}} + \underbrace{\sum_{i < j < k} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k)}_{\text{3-body interactions}} = \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_{ij}), \quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j.$$

Note that

$$U = \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_{ij}) = \sum_{i < j} U_2(\vec{r}_{ij}).$$

4.1 Morse potential (diatomic molecule)

$$U_2(r) = U_M(r) = U_\infty + D_e \left\{ [1 - e^{-\alpha(r-r_0)}]^2 - 1 \right\}$$

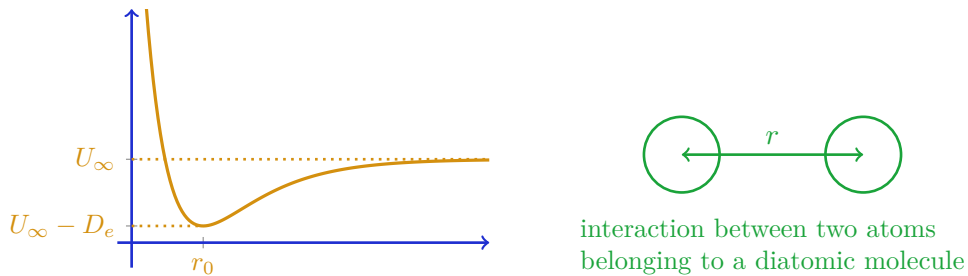


Figure 4.2: Morse potential $U_M(r)$ and the two atoms of a diatomic molecule at distance r .

$$\left. \frac{dU_M}{dr} \right|_{r=r_0} = 0 \quad \text{and} \quad U_M(r_0) = U_\infty - D_e.$$

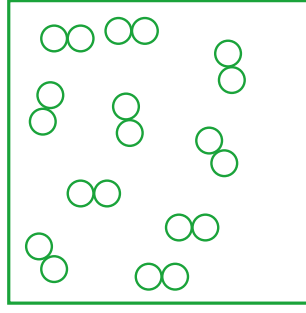


Figure 4.3: Interaction of pairs of particles belonging to a diatomic molecule: a fluid of diatomic molecules.

4.2 Polymers

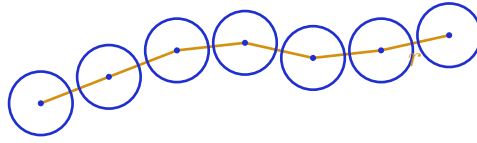


Figure 4.4: A polymer: a chain of particles (monomers); r is the distance between two successive monomers.

$$U_{\text{FENE}}(r) = \begin{cases} -\frac{1}{2} r_{\text{max}}^2 \epsilon \ln \left[1 - \left(\frac{r}{r_{\text{max}}} \right)^2 \right] & r \leq r_{\text{max}} \\ \infty & r > r_{\text{max}} \end{cases}$$

Interactions of two successive particles belonging to a polymer.

FENE = {Finite Extensible Non-linear Elastic}.

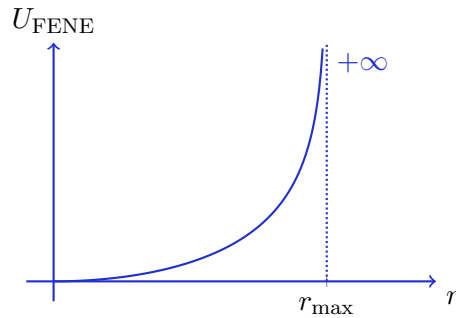


Figure 4.5: FENE potential: it diverges at $r = r_{\text{max}}$.

If $r \ll r_{\text{max}}$:

$$U_{\text{FENE}} \simeq \epsilon \frac{r^2}{2},$$

hence ϵ is the elastic constant of small oscillations.

4.3 Lennard-Jones

(Noble gases such as argon, neon, xenon or radon) [monoatomic gases]

[1964 Rahman and 1969 Verlet and Hansen]

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

$$r_m = 2^{1/6} \sigma \simeq 1.12 \sigma, \quad U_{LJ}(r_m) = -\epsilon.$$

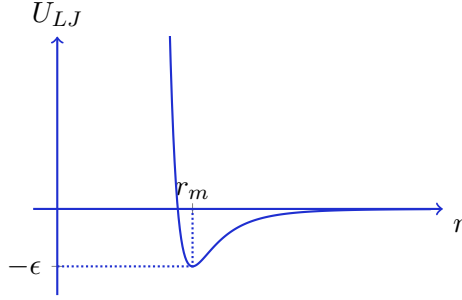


Figure 4.6: Lennard-Jones potential, with minimum $-\epsilon$ at $r_m = 2^{1/6} \sigma$.

This potential well describes the interaction between uncharged atoms.

4.4 Soft sphere potential

$$U_{SS}(r) = \epsilon \left(\frac{\sigma}{r} \right)^n \quad [n \text{ quantifies the softness of the particles}]$$

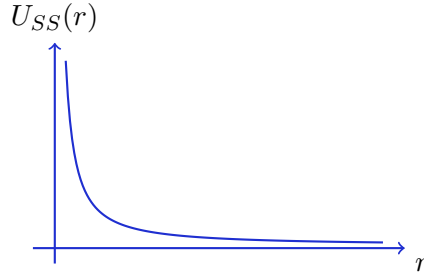


Figure 4.7: Soft sphere potential (purely repulsive).

4.5 Scaling laws of soft-sphere fluid

$$F = -k_B T \ln Z, \quad Z = \int_V e^{-\beta U_{SS}} d^{3N} r,$$

$$U_{SS} = \epsilon \sum_{i < j} \left(\frac{\sigma}{r_{ij}} \right)^n, \quad r_{ij} = |\vec{r}_{ij}|,$$

$$Z = \int_V e^{-\beta \epsilon \sum_{i < j} \left(\frac{\sigma}{r_{ij}} \right)^n} d^{3N} r.$$

Scaled coordinates: $\vec{r}_i = V^{1/3} \vec{\xi}_i$, so that

$$Z = \int_V \exp \left[- \underbrace{\frac{\beta \epsilon \sigma^n}{V^{n/3}}}_{\downarrow} \sum_{i < j} \left(\frac{1}{\xi_{ij}} \right)^n \right] V^N d^{3N} \xi.$$

Consider

$$\frac{\beta \varepsilon \sigma^n}{V^{n/3}} = \left[(\beta \varepsilon)^{3/n} \sigma^3 \underbrace{\frac{N}{V}}_{=\rho} \right]^{n/3} \frac{1}{N^{n/3}}.$$

If we define

$$\Gamma \equiv (\beta \varepsilon)^{3/n} \sigma^3 \rho = \Gamma(T, \rho)$$

we have

$$\begin{aligned} Z &= V^N \int e^{-\left(\frac{\Gamma}{N}\right)^{n/3} \sum_{i<j} \left(\frac{1}{\xi_{ij}}\right)^n} d^{3N} \xi \\ &= Z_{\text{ID}} \cdot Z_{\text{EX}}(\Gamma) \end{aligned}$$

where $Z_{\text{ID}} = V^N$ and

$$Z_{\text{EX}}(\Gamma) = \int e^{-\left(\Gamma/N\right)^{n/3} \sum_{i<j} \left(\frac{1}{\xi_{ij}}\right)^n} d^{3N} \xi.$$

For the internal energy:

$$U = U_{\text{ID}} + U_{\text{EX}}, \quad U_{\text{ID}} = \langle K \rangle = \frac{3}{2} N k_B T,$$

$$\begin{aligned} \beta U_{\text{EX}} &= \beta \langle U_{SS} \rangle = \beta \int U_{SS} \frac{e^{-\beta U_{SS}}}{Z} d^{3N} r \\ &= \int \widetilde{\beta U_{SS}} \frac{e^{-\widetilde{\beta U_{SS}}}}{V^N Z_{\text{EX}}(\Gamma)} V^N d^{3N} \xi. \end{aligned}$$

But

$$\beta U_{SS} = \left(\frac{\Gamma}{N}\right)^{n/3} \sum_{i<j} \left(\frac{1}{\xi_{ij}}\right)^n = f(\Gamma) \quad [\text{for fixed } N]$$

hence

$$\beta U_{\text{EX}} = \mathcal{F}(\Gamma).$$

Simulations with the same $\Gamma = \Gamma(T, \rho)$ (even if T and ρ are different) will yield the same value of βU_{EX} , i.e.

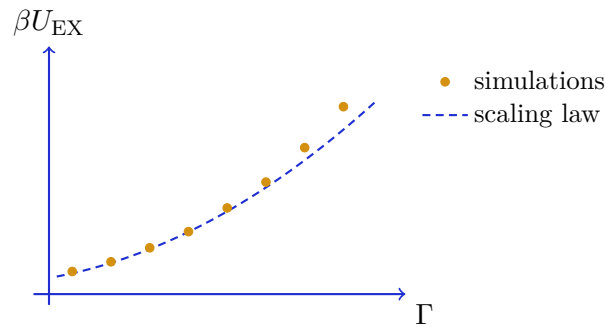


Figure 4.8: βU_{EX} as a function of Γ : simulations at different (T, ρ) but equal Γ fall on the same curve.

Note that: $F = -k_B T \ln Q$, but $Q = \frac{\Lambda^{-3N}}{N!} Z$ and $\frac{\Lambda^{-3N}}{N!}$ does not depend on V .

Similar scaling for the pressure:

$$P = -\frac{\partial F}{\partial V} = \boxed{\frac{\partial (k_B T \ln Z)}{\partial V}}, \quad \text{but } Z = \underbrace{Z_{\text{ID}}}_{=V^N} \cdot Z_{\text{EX}},$$

$$P = \underbrace{\frac{\partial}{\partial V} [k_B T N \ln V]}_{P_{\text{ID}}} + \underbrace{k_B T \frac{1}{Z_{\text{EX}}} \frac{\partial Z_{\text{EX}}}{\partial V}}_{P_{\text{EX}}},$$

$$P = P_{\text{ID}} + P_{\text{EX}} = \frac{\rho}{\beta} + P_{\text{EX}}, \quad P_{\text{ID}} = \rho k_B T,$$

$$P_{\text{EX}} = k_B T \frac{1}{Z_{\text{EX}}} \frac{\partial Z_{\text{EX}}}{\partial V} = k_B T \frac{1}{Z_{\text{EX}}} \frac{\partial Z_{\text{EX}}}{\partial \Gamma} \frac{\partial \Gamma}{\partial V}.$$

But

$$\frac{\partial \Gamma}{\partial V} = -(\beta \varepsilon)^{3/n} \frac{N}{V^2} \sigma^3 = -\Gamma \frac{\rho}{N},$$

so that

$$P_{\text{EX}} = \rho k_B T \underbrace{\left(-\frac{\Gamma/N}{Z_{\text{EX}}(\Gamma)} \frac{\partial Z_{\text{EX}}}{\partial \Gamma} \right)}_{G(\Gamma)} \quad [G \text{ depends only on } \Gamma \text{ for fixed } N]$$

and

$$\frac{\beta P_{\text{EX}}}{\rho} = G(\Gamma) \quad \text{scaling law.}$$

If one performs simulations changing T and ρ but at fixed Γ , one has to get the same value of $\beta P_{\text{EX}}/\rho$:

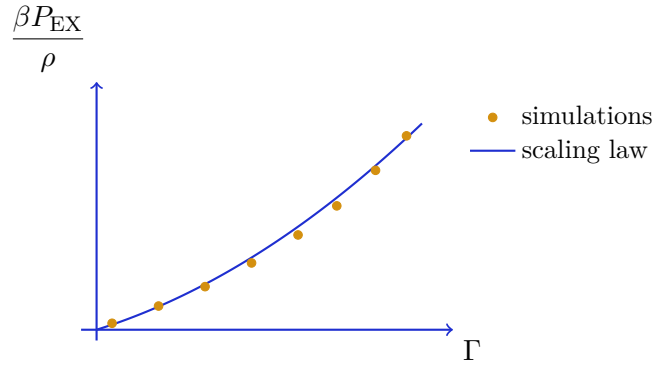


Figure 4.9: $\beta P_{\text{EX}}/\rho$ as a function of Γ : simulations versus scaling law.

4.6 Coulomb interactions

$$U_C(r) = \frac{1}{4\pi \varepsilon_r \varepsilon_0} \frac{q_i q_j}{r}$$

Screened interactions [Debye–Hückel theory]:

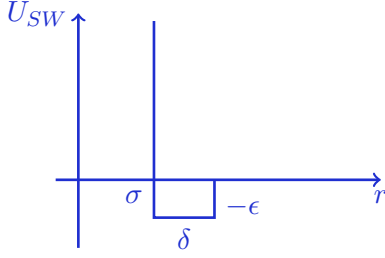
$$U_{SC}(r) = A \frac{q_i q_j}{r} e^{-r/\lambda},$$

where λ is the Debye screening length; λ depends on the charges in solution.

4.7 Hard spheres and square well

Hard spheres (already discussed).

Square well:



$$U_{SW} = \begin{cases} +\infty & r < \sigma \\ -\epsilon & \sigma < r < \sigma + \delta \\ 0 & r > \sigma + \delta \end{cases}$$

4.8 Truncation, shift and smoothing of interaction potentials

Interaction potentials may extend to infinite distance (e.g. Lennard-Jones), hence the need of truncation:

$$U_{LJ}^c(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r \leq r_c \\ 0 & r > r_c \end{cases}$$

where r_c is the cutoff radius (in old literature $r_c = 2.5\sigma$).

At $r = r_c$ we have a discontinuity (bad for MD simulations, as we shall see), hence shift of the potential, i.e.

$$U_{LJ}^{cs}(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Note that for MC simulations the shift is not needed.

Modified LJ

To have also the first derivative continuous:

$$U_{LJ}^M = \begin{cases} U_{LJ}(r) + ar + b & r \leq r_c \\ 0 & r > r_c \end{cases}$$

where a and b are such that

$$\begin{aligned} U_{LJ}(r_c) + ar_c + b &= 0, \\ \frac{dU_{LJ}^M}{dr} \Big|_{r=r_c} &= \frac{dU_{LJ}(r)}{dr} \Big|_{r=r_c} + a = 0, \end{aligned}$$

so that

$$a = -\frac{dU_{LJ}}{dr} \Big|_{r=r_c}, \quad b = -U_{LJ}(r_c) - ar_c.$$

Typically $2.5\sigma \leq r_c \leq 5\sigma$.

Switch function

$$U_{LJ}^S(r) = U_{LJ}(r) \cdot S(r)$$

where

$$S(r) = 0.5 \left[1 + \tanh \left(\frac{r_c - r}{\delta} \right) \right], \quad \tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad \text{with } \delta \ll r_c.$$

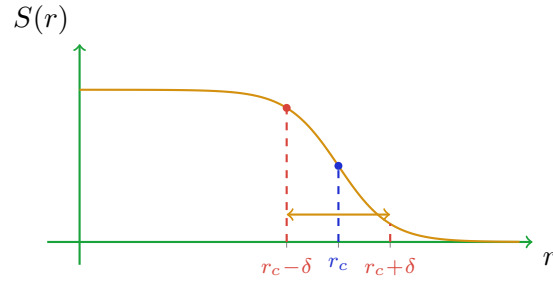


Figure 4.10: Switch function $S(r)$. By δ one can set the extent of the “switching” interval ($\delta \ll r_c$).

Lennard-Jones potential from first principles

[see slides]

4.8.1 Example: simulation of a polymer melt (Kremer–Grest model)

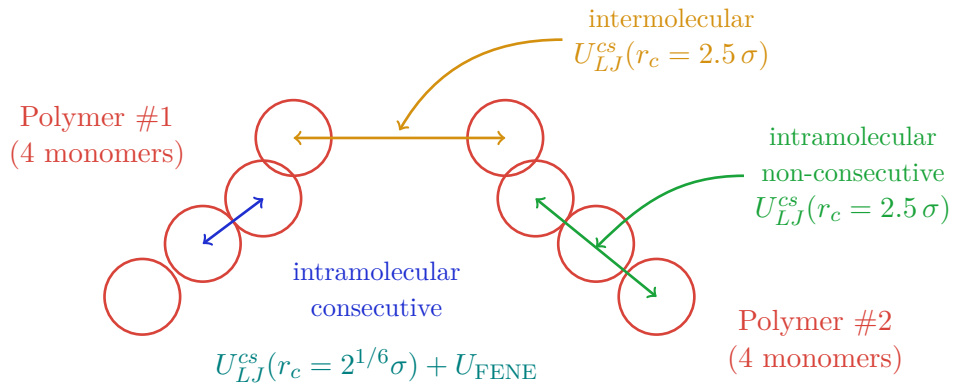


Figure 4.11: Kremer–Grest model of a polymer melt: interactions between monomers.

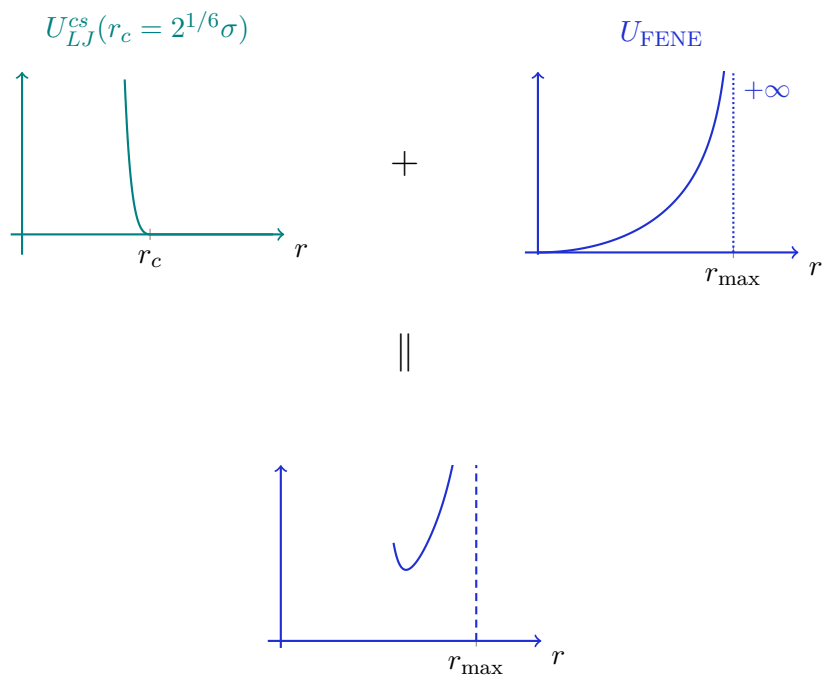


Figure 4.12: Bonded (consecutive) monomers: the purely repulsive truncated and shifted LJ plus the FENE potential give an effective potential with a minimum, diverging both at small r and at $r = r_{\text{max}}$.

Chapter 5

Setting up a simulation

5.1 Surface effects

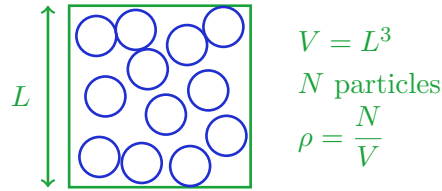


Figure 5.1: N particles in a cubic box of side L .

$$F = F_{\text{surf}} + F_{\text{bulk}}$$

$$F_{\text{surf}} = \gamma \underbrace{\sigma}_{[\text{area}]} = 6\gamma L^2, \quad F_{\text{bulk}} = \underbrace{\kappa}_{[\text{constant}]} \cdot N = \kappa \rho V = \kappa \rho L^3.$$

Hence

$$\frac{F_{\text{surf}}}{F_{\text{bulk}}} \sim \frac{1}{L},$$

i.e. F_{surf} is not negligible for simulated systems, since the box size is rather small.

Need to get rid of surface effects to compare with experimental results.

5.1.1 Infinite replicas of the system

$$U = \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_{ij}) \quad [U: \text{potential energy}; U_2: \text{pair potential}]$$

$\Downarrow$

$$U = \frac{1}{2} \sum_{\substack{i,j,\vec{n} \\ i \neq j \text{ if } \vec{n}=0}} U_2(\vec{r}_i - (\vec{r}_j + L \vec{n}))$$

where

$$\vec{n} = (n_x, n_y, n_z), \quad n_\alpha \text{ signed integer}, \quad \alpha = x, y, z.$$

Problem: infinite terms in the calculation of the energy

$\Downarrow$

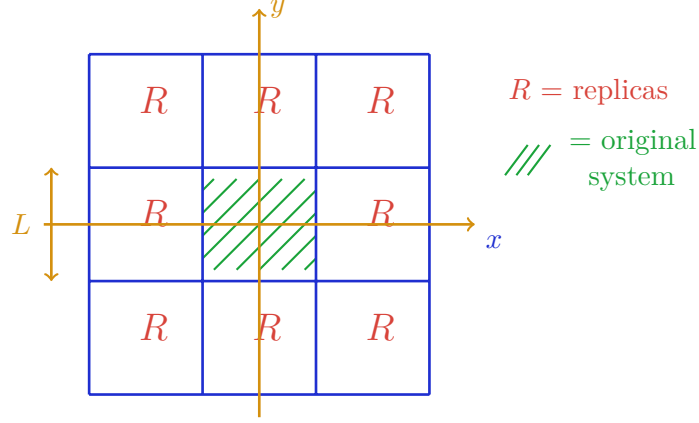


Figure 5.2: The original system (hatched) surrounded by its periodic replicas R .

5.1.2 Minimum image convention

When we move a particle i in a MC simulation we need to calculate the variation of U , i.e.

$$\Delta U_i = U'_i - U_i, \quad \vec{r}_i \rightarrow \vec{r}'_i \uparrow \text{[new state]}$$

where

$$U'_i = \sum_j U_2(\vec{r}'_i - \vec{r}_j),$$

$$U_i = \sum_j U_2(\vec{r}_i - \vec{r}_j).$$

To calculate U_i and U'_i we employ the minimum image convention.

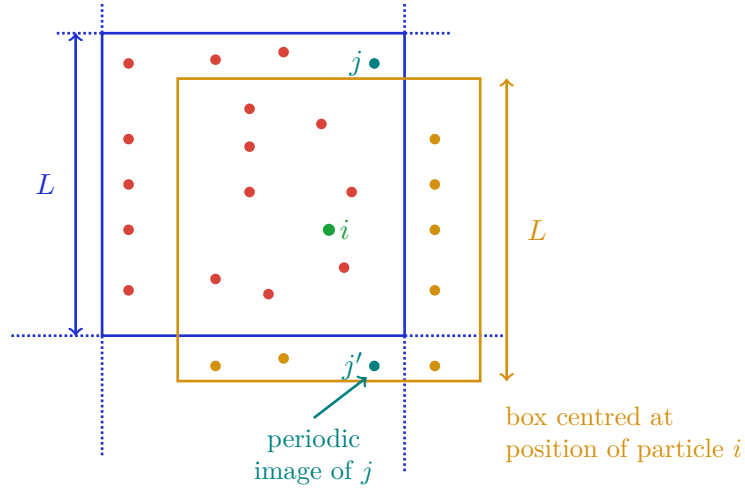


Figure 5.3: Minimum image convention: only the particles (or their periodic images) inside the box of side L centred at particle i are considered; j' is the periodic image of j .

Energy:

$$U_i = \sum_j U_2(\vec{r}_i - \vec{r}_j)$$

[the sum runs over all j within the box of size L centred at the position of particle i], where we require

$$r_c < \frac{L}{2}$$

so that we are not missing contributions.

$$U_i = \sum_j U_2(\vec{r}_i - \vec{r}_j) = \sum_j U_2(\vec{r}_{ij})$$

If j is not inside the minimum image we need to consider its periodic image, i.e. this amounts to doing this replacement:

$$U_2(\vec{r}_{ij}) \longrightarrow U_2\left(\vec{r}_{ij} - L \cdot \underset{\substack{\uparrow \\ \text{[element-wise division]}}}{\text{rint}\left(\frac{\vec{r}_{ij}}{L}\right)}\right) \quad (*)$$

where, if $\vec{v} = (v_x, v_y, v_z)$,

$$\text{rint}(\vec{v}) \equiv \text{rint} \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \equiv \begin{pmatrix} \text{rint}(v_x) \\ \text{rint}(v_y) \\ \text{rint}(v_z) \end{pmatrix}$$

where

$$\text{rint}(x) = \{\text{integer nearest to } x\}.$$

Examples:

$$\text{rint}(0.6) = 1, \quad \text{rint}(0.2) = 0, \quad \text{rint}(-0.7) = -1.$$

Let's show that $(*)$ provides the correct minimum image particle (i.e. the particle j in the periodic system which is closest to i).

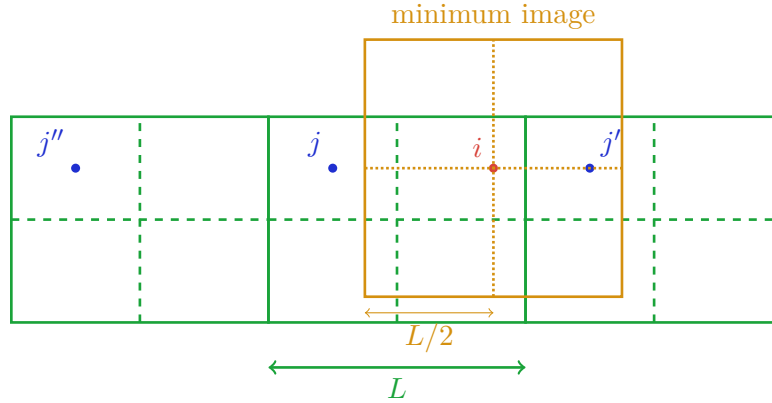


Figure 5.4: The particle j , its periodic images j' and j'' , and the minimum image box centred at i : the closest image of j to i is j' .

Let

$$\begin{aligned} \vec{r}_i &= (x_i, y_i), & \vec{r}_j &= (x_j, y_j), \\ \vec{r}_i - \vec{r}_j - L \text{rint}\left(\frac{\vec{r}_i - \vec{r}_j}{L}\right) &= ? \end{aligned}$$

But (for the configuration in the figure)

$$L \text{rint}\left(\frac{\vec{r}_i - \vec{r}_j}{L}\right) = L \text{rint}\left(\begin{pmatrix} \frac{x_i - x_j}{L} \\ \frac{y_i - y_j}{L} \end{pmatrix}\right) = L \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} L \\ 0 \end{pmatrix} \quad \text{[element-wise division]}$$

hence

$$\begin{pmatrix} x_i - x_j - L \\ y_i - y_j \end{pmatrix} = \begin{pmatrix} x_i - (x_j + L) \\ y_i - y_j \end{pmatrix} = \begin{pmatrix} x_i - x_{j'} \\ y_i - y_{j'} \end{pmatrix} = \vec{r}_i - \underset{\substack{\uparrow \\ \text{[closest periodic image of } j]}}{\vec{r}_{j'}}.$$

Final remark: the adjustment of distances between particles (eq. $(*)$) must be applied every time one has to calculate distances for the calculation of the interaction potential.

5.2 Initial configuration

5.2.1 Cubic lattice

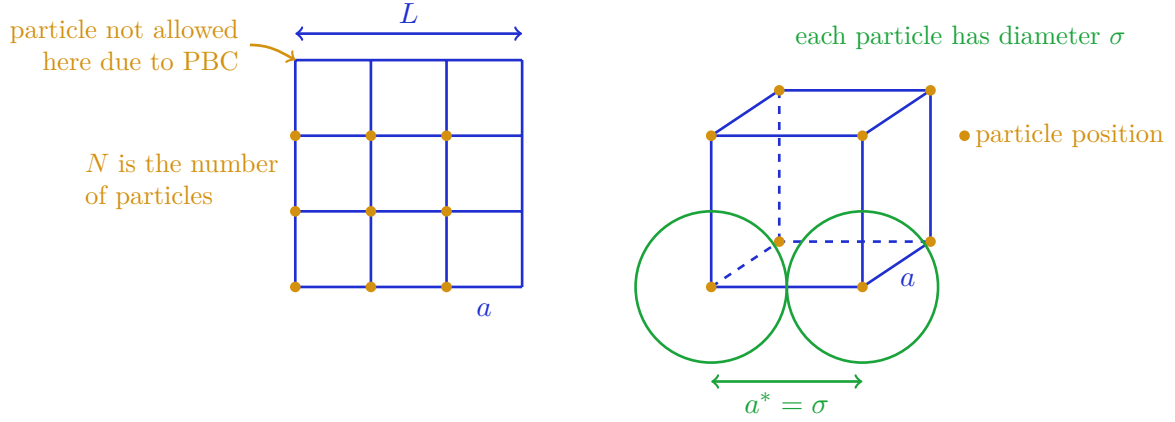


Figure 5.5: Simple cubic lattice: 2D view of the box (left) and unit cell of side a (right); a^* is the minimum value of a .

$$\phi = \frac{N v_0}{L^3} = \frac{\overbrace{n \left(\frac{L}{a}\right)^3}^N v_0}{L^3} = \frac{n v_0}{a^3}$$

where v_0 is the volume of a particle and n is the number of particles per unit cell ($n = 1$ in this case). But

$$v_0 = \frac{\pi}{6} \sigma^3 \quad \text{if the particle is spherical,}$$

hence, considering that $a^* = \sigma$,

$$\phi^* = \{\text{maximum } \phi\} = \frac{v_0}{(a^*)^3} = \frac{\pi}{6} \frac{\cancel{\sigma^3}}{\cancel{\sigma^3}} = \frac{\pi}{6}.$$

If we want a lower $\phi = \phi'$ it is just a matter of expanding the box and scaling the particle positions by a factor ξ such that

$$L' = \xi L, \quad \vec{r}'_i = \xi \vec{r}_i, \quad \text{with } \xi = \left(\frac{\phi^*}{\phi'}\right)^{1/3}, \quad \text{i.e. } \phi' = \frac{\phi^*}{\xi^3}.$$

5.2.2 Higher ϕ : body centred cubic (BCC)

$$\phi^* = \frac{n v_0}{(a^*)^3}$$

where in this case $n = 2$ and a^* is such that

$$\overline{AB} = \sigma = \frac{\sqrt{3} a^*}{2}, \quad \text{i.e.} \quad a^* = \frac{2}{\sqrt{3}} \sigma,$$

so that

$$\phi^* = \frac{2 \frac{\pi}{6} \cancel{\sigma^3}}{\left(\frac{2}{\sqrt{3}}\right)^3 \cancel{\sigma^3}} = \frac{\pi}{3} \left(\frac{\sqrt{3}}{2}\right)^3 \approx 0.68.$$

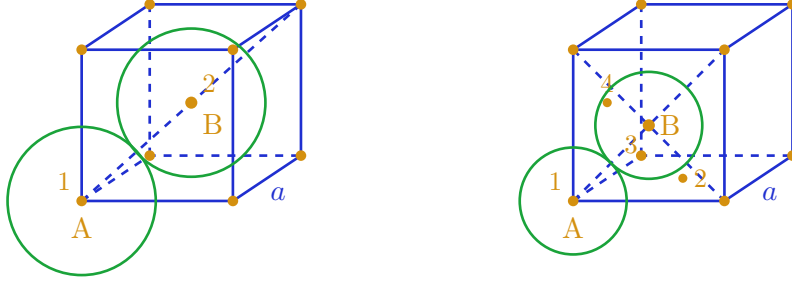


Figure 5.6: Unit cells of the BCC (left) and FCC (right) lattices; the green spheres of diameter σ around the nearest neighbours A and B are in contact for $a = a^*$.

5.2.3 Even higher ϕ : face centred cubic (FCC)

$$\phi^* = \frac{n v_0}{(a^*)^3}$$

where in this case $n = 4$ and a^* is such that

$$\overline{AB} = \sigma = \frac{\sqrt{2}}{2} a^*, \quad \text{i.e.} \quad a^* = \frac{2}{\sqrt{2}} \sigma,$$

so that

$$\phi^* = \frac{4 \frac{\pi}{6} \cancel{\sigma^3}}{\left(\frac{2}{\sqrt{2}}\right)^3 \cancel{\sigma^3}} = 2 \left(\frac{\sqrt{2}}{2}\right)^3 \frac{\pi}{3} \approx 0.74.$$

5.3 Linked cell lists

In a Metropolis MC a MC step consists of attempting to move N particles. For each particle

$$\text{acc}(o \rightarrow n) = \min\{1, e^{-\beta \Delta U}\}, \quad \Delta U = U'_i - U_i,$$

where

$$U_i = \sum_j v_2(\vec{r}_{ij}),$$

which requires N calculations of v_2 [note that even if $r > r_c$ we need to calculate $|\vec{r}|$]. Hence for a MC step the complexity is

$$\mathcal{O}(N \times N) = \mathcal{O}(N^2).$$

We want to reduce the number of times we have to calculate v_2 .

Let's consider M^3 cubic cells such that

$$\frac{L}{M} \geq r_c \quad (r_c: \text{cutoff radius}),$$

i.e. M is the largest integer such that $\ell = L/M > r_c$.

To calculate U_i and U'_i we can just consider the particles in the 27 cells (i.e. the cell to which particle i belongs and the 26 adjacent cells).

If an accepted move takes particle i into a different cell, the linked cells must be updated accordingly: i is removed from the list of its old cell and inserted in the list of the new one.

With this strategy for each MC step we have to calculate $\tilde{N}$ times v_2 , with

$$\tilde{N} \approx N \cdot 27 \cdot r_c^3 \rho = N \underbrace{27 r_c^3 \rho}_{\text{this is a constant if we increase the box size keeping } \rho \text{ fixed}} = \mathcal{O}(N).$$

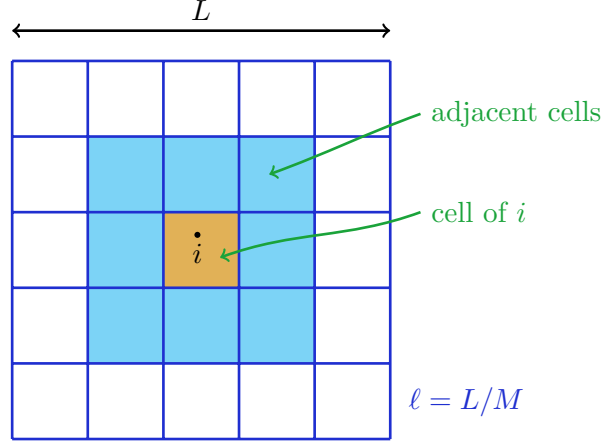


Figure 5.7: Linked cells (2D sketch): the cell of particle i and its adjacent cells.

5.4 Nearest neighbour lists (NNL)

Consider two particles i and j and observe that:

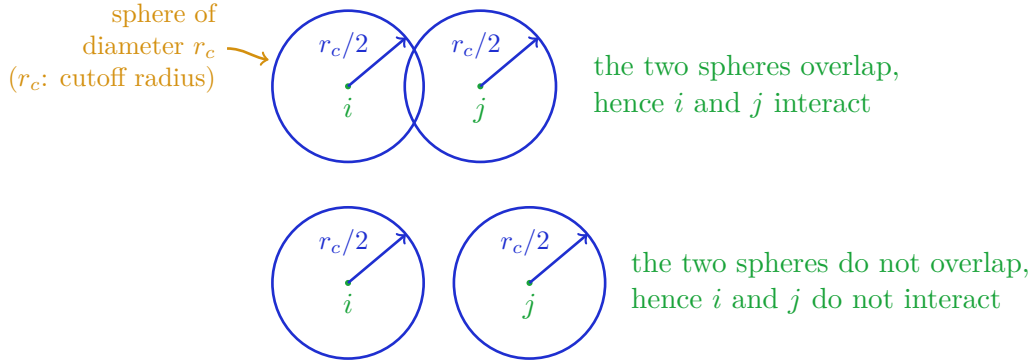


Figure 5.8: Two particles interact if and only if their spheres of diameter r_c (radius $r_c/2$) overlap.

At a certain time t_0 (MC step) we build the NNL of all particles (starting from the first simulation step).

Consider the building of the NNL of a particle i ; j and j' are two particles other than i .

$$\begin{aligned} \text{NNL}(i) &= \{\text{list of all particles belonging to the NNL of } i\} \\ &= \{\text{all particles which have outer spheres overlapping with that of } i\}. \end{aligned}$$

Hence in this case:

$$j \in \text{NNL}(i), \quad j' \notin \text{NNL}(i),$$

since the spheres of radius $\frac{r_c}{2} + \Delta$ overlap (for j) and do not overlap (for j').

For $t > t_0$ the inner spheres are placed with their centre at the particle position, while the outer spheres are kept fixed. As long as each inner sphere remains inside its corresponding outer sphere we can calculate U_i and U'_i by considering, $\forall i$, the particles $\in \text{NNL}(i)$,

since if two inner spheres are inside two non-overlapping outer spheres they cannot overlap (and the corresponding particles cannot interact).

An inner sphere escapes if

$$\|\vec{r}_i(t) - \vec{r}_i(t_0)\| \geq \Delta.$$

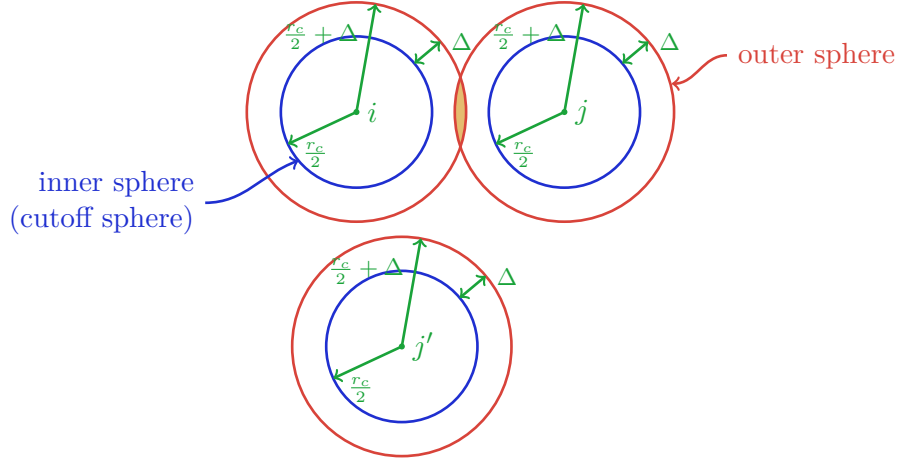


Figure 5.9: Inner (cutoff) spheres of diameter r_c (radius $r_c/2$) and outer spheres of radius $r_c/2 + \Delta$ for particles i , j and j' ; the outer spheres of i and j overlap.

If this happens all the NNL must be rebuilt.

Δ is a parameter which must be optimized.

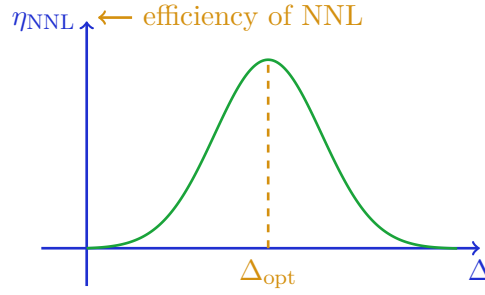


Figure 5.10: Efficiency of the NNL as a function of Δ .

And if η_{LL} is the efficiency of LL

$$\frac{\eta_{\text{NNL}}}{\eta_{\text{LL}}} = \frac{\{\# \text{ particles in the 27 LL cells}\}}{\{\# \text{ particles in the NNL}(i)\}} \approx \frac{\rho r_c^3 27}{\underbrace{\frac{4\pi}{3} r_c^3 \rho}_{\text{if } \Delta \ll r_c}} \approx \frac{27 \cdot 3}{4\pi} \approx 6$$

[since for each particle we need to test if $r < r_c$]

Chapter 6

Measuring observables

6.1 Radial distribution function

$\tilde{\rho}(\vec{r}_1, \vec{r}_2) = \{\text{probability of finding a particle in } \vec{r}_1 \text{ and another one in } \vec{r}_2\}.$

Let

event $A = \{\text{a particle is in } \vec{r}_1\},$

event $B = \{\text{a particle is in } \vec{r}_2\}.$

Then

$$P(A \cap B) = \tilde{\rho}(\vec{r}_1, \vec{r}_2), \quad P(A \cap B) = \underbrace{P(A|B)}_{\text{conditional probability}} \cdot P(B),$$

i.e.

$$P(A|B) = \frac{P(A \cap B)}{P(B)}.$$

Note that (homogeneous case): if $P(A) = P(B),$

$$P(A|B) = \frac{P(A \cap B)}{P(B)} = \frac{P(A \cap B)}{P(A)} = P(B|A).$$

If A and B are independent,

$$P(A|B) = \frac{P(A) \cancel{P(B)}}{\cancel{P(B)}} = P(A).$$

Going back to $\tilde{\rho}$:

$$\tilde{\rho}(\vec{r}_1, \vec{r}_2) = \tilde{\rho}(\vec{r}_1|\vec{r}_2) \tilde{\rho}(\vec{r}_2) \quad (*)$$

We define:

$$g^{(2)}(\vec{r}_1, \vec{r}_2) \equiv \frac{\tilde{\rho}(\vec{r}_1, \vec{r}_2)}{\tilde{\rho}(\vec{r}_1) \tilde{\rho}(\vec{r}_2)} \quad \leftarrow \text{this is the 2-particle (pair) distribution function.}$$

If the system is homogeneous $\tilde{\rho}(\vec{r}_1) = \tilde{\rho}(\vec{r}_2) = \tilde{\rho}$, so that

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\tilde{\rho}(\vec{r}_1, \vec{r}_2)}{\tilde{\rho}^2}.$$

But using $(*)$ we have:

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\tilde{\rho}(\vec{r}_1|\vec{r}_2) \cancel{\tilde{\rho}}}{\tilde{\rho} \cancel{\tilde{\rho}}} = \frac{\tilde{\rho}(\vec{r}_1|\vec{r}_2)}{\tilde{\rho}},$$

i.e.

$$\tilde{\rho} g^{(2)}(\vec{r}_1, \vec{r}_2) = \tilde{\rho}(\vec{r}_1 | \vec{r}_2).$$

Since the system is homogeneous we can expect $g^{(2)}(\vec{r}_1, \vec{r}_2) = g^{(2)}(\vec{r}_1 - \vec{r}_2)$, so that $g^{(2)}(\vec{r}_1 - \vec{r}_2) = g^{(2)}(\vec{r})$ and $\tilde{\rho}(\vec{r}_1 | \vec{r}_2) = \tilde{\rho}(\vec{r})$.

Ideal gas.

$$\tilde{\rho}(\vec{r}_1 | \vec{r}_2) = \tilde{\rho}(\vec{r}_1) = \tilde{\rho},$$

hence

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\tilde{\rho}}{\tilde{\rho}} = 1.$$

Hard spheres. If $\|\vec{r}_1 - \vec{r}_2\| < \sigma \implies \tilde{\rho}(\vec{r}_1 | \vec{r}_2) = 0$ and $g^{(2)}(\vec{r}_1, \vec{r}_2) = 0$. Moreover the system is isotropic, therefore

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = g^{(2)}(\|\vec{r}_{12}\|) = \underbrace{g^{(2)}(r)}_{\text{radial distribution function}}.$$

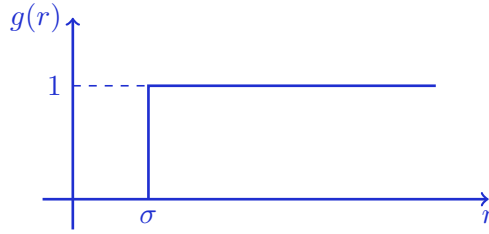


Figure 6.1: Radial distribution function of hard spheres at very low densities.

This holds at very low densities. But at high densities? We will see...

6.1.1 Two-point density

If

$$\mathcal{N}(\vec{r}_1, \dots, \vec{r}_N) = \frac{e^{-\beta U_N}}{Z},$$

$\mathcal{N}(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N$ is the probability of finding particles at positions $\vec{r}_1, \dots, \vec{r}_N$. Hence the probability density to find one particle in $\vec{r}_1$ is:

$$\tilde{\rho}(\vec{r}_1) = \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_2 \cdots d\vec{r}_N \quad (\text{note that we are not integrating over } d\vec{r}_1)$$

and the (1-particle) density is:

$$\rho(\vec{r}_1) = \underbrace{N}_{\text{total number of particles}} \cdot \tilde{\rho}(\vec{r}_1) = N \cdot \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_2 \cdots d\vec{r}_N.$$

Note that

$$\int \tilde{\rho}(\vec{r}_1) d\vec{r}_1 = 1$$

and that

$$N \tilde{\rho}(\vec{r}_1) d\vec{r}_1 = \{\text{number of particles in } d\vec{r}_1\}.$$

Moreover, if the system is homogeneous,

$$\rho(\vec{r}_1) = \frac{N}{V}.$$

Similarly the probability density of finding a particle in $\vec{r}_1$ and $\vec{r}_2$ is

$$\tilde{\rho}(\vec{r}_1, \vec{r}_2) = \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_3 \cdots d\vec{r}_N \quad (\text{note that we are not integrating over } \vec{r}_1 \text{ and } \vec{r}_2),$$

so that

$$\underbrace{N(N-1)}_{\substack{\text{total number} \\ \text{of possible pairs}}} \tilde{\rho}(\vec{r}_1, \vec{r}_2) = \{\text{number of pairs in } d\vec{r}_1 \text{ and } d\vec{r}_2\}$$

and we define the two-particle density as follows:

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \int \frac{e^{-\beta U_N}}{Z} d^{(N-2)}\vec{r}.$$

Ideal gas.

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_3 \cdots d\vec{r}_N, \quad U_N = 0,$$

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \int \frac{d\vec{r}_3 \cdots d\vec{r}_N}{Z} = N \overbrace{(N-1)}^{\simeq N} \frac{V^{N-2}}{V^N} \simeq \frac{N^2}{V^2} = \rho^2,$$

since $Z = \int e^{-\beta U_N} d\vec{r}_1 \cdots d\vec{r}_N = V^N$. Hence

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\rho^{(2)}(\vec{r}_1, \vec{r}_2)}{\rho^2} = \frac{\rho^2}{\rho^2} = 1.$$

6.1.2 Alternative ways of calculating 1-point and 2-point densities

$$\begin{aligned} \rho(\vec{r}) &= \frac{N}{Z} \int e^{-\beta U_N} d^{(N-1)}\vec{r} & U_N &= U_N(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \\ &= \frac{N}{Z} \int e^{-\beta U_N} \delta(\vec{r} - \vec{r}_1) d^N \vec{r} & \text{now } U_N &= U_N(\vec{r}_1, \dots, \vec{r}_N) \\ &= \frac{1}{Z} \sum_i^N \int e^{-\beta U_N} \delta(\vec{r} - \vec{r}_i) d^N \vec{r} & \text{the integral does not depend on the particle index} \\ &= \left\langle \sum_i^N \delta(\vec{r} - \vec{r}_i) \right\rangle. \end{aligned}$$

To see that the integral does not depend on the particle index, take a system of 3 particles, consider $\vec{r}_2$ and $\vec{r}_3$ instead of $\vec{r}_1$, then swap the indices to recover the case above ($\vec{r}_1$). Note that $U_2(\vec{r}_{ij}) = U_2(\vec{r}_{ji})$. Here

$$\langle \dots \rangle = \int \dots \frac{e^{-\beta U_N}}{Z} d^N \vec{r}.$$

Similarly

$$\rho^{(2)}(\vec{r}', \vec{r}) = \left\langle \sum_{i,j}' \delta(\vec{r}' - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \right\rangle, \quad \sum' : i \neq j.$$

Indeed

$$\begin{aligned} \rho^{(2)}(\vec{r}', \vec{r}) &= N(N-1) \int \frac{e^{-\beta U_N}}{Z} d^{(N-2)}\vec{r} & U_N &= U_N(\vec{r}', \vec{r}, \vec{r}_3, \dots, \vec{r}_N) \\ &= N(N-1) \int \delta(\vec{r}' - \vec{r}_1) \delta(\vec{r} - \vec{r}_2) \frac{e^{-\beta U_N}}{Z} d\vec{r}_1 d\vec{r}_2 d^{(N-2)}\vec{r} & U_N &= U_N(\vec{r}_1, \dots, \vec{r}_N) \\ &= \sum_{i,j}' \int \delta(\vec{r}' - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \frac{e^{-\beta U_N}}{Z} d^N \vec{r}, \end{aligned}$$

since the integral does not depend on which pair of indices we are considering (take again a system of 3 particles and use $(\vec{r}_2, \vec{r}_3)$ instead of $(\vec{r}_1, \vec{r}_2)$). Therefore

$$\rho^{(2)}(\vec{r}', \vec{r}) = \left\langle \sum'_{i,j} \delta(\vec{r}' - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \right\rangle$$

6.1.3 $\rho^{(2)}(\vec{r}', \vec{r})$ in the homogeneous case

Let's consider

$$\begin{aligned} \left\langle \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r} - \underbrace{(\vec{r}_i - \vec{r}_j)}_{\vec{r}_{ij}}) \right\rangle &= \left\langle \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r} - \vec{r}_i + \vec{r}_j) \right\rangle \\ &= \left\langle \frac{1}{N\rho} \int \sum'_{i,j} \delta(\vec{r} - \vec{r}_i + \vec{r}') \delta(\vec{r}' - \vec{r}_j) d\vec{r}' \right\rangle \\ &= \frac{1}{N\rho} \int \overbrace{\left\langle \sum'_{i,j} \delta((\vec{r} + \vec{r}') - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle}^{\rho^{(2)}(\vec{r} + \vec{r}', \vec{r}')} d\vec{r}' \end{aligned}$$

(a function of $\vec{r}$, and we average over $\vec{r}_1, \dots, \vec{r}_N$)

$$\dots = \frac{1}{N\rho} \int \rho^{(2)}(\vec{r} + \vec{r}', \vec{r}') d\vec{r}'.$$

But the system is homogeneous, therefore $\rho^{(2)}(\vec{r} + \vec{r}', \vec{r}') = \rho^{(2)}(\vec{r})$, i.e. it is independent of $\vec{r}'$:

$$= \frac{1}{N\rho} \int \rho^{(2)}(\vec{r}) d\vec{r}' = \frac{V}{N\rho} \rho^{(2)}(\vec{r}) = \frac{1}{\rho^2} \rho^{(2)}(\vec{r}) = \frac{g^{(2)}(\vec{r}) \rho^2}{\rho^2} = g^{(2)}(\vec{r}).$$

We proved that

$$g^{(2)}(\vec{r}) = \frac{1}{N\rho} \left\langle \sum'_{i,j} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \right\rangle = \frac{1}{N\rho} \left\langle \sum'_{i,j} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle, \quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j.$$

6.1.4 Average value of $g(\vec{r})$ over a volume ΔV around $\vec{r}$

$$\bar{g}(\vec{r}) = \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} g(\vec{r}') d\vec{r}',$$

where the subscript in $\Delta V_{\vec{r}}$ is to remind that the volume ΔV is around $\vec{r}$. $\bar{g}$ is dependent on the chosen $\Delta V_{\vec{r}}$ (if $\Delta V_{\vec{r}}$ is a cubic box, $\bar{g}$ depends on its position $\vec{r}$).

In a MC simulation:

$$\langle \mathcal{O}(\vec{r}^N) \rangle = \frac{1}{L} \sum_{\underbrace{k=1}}^L \mathcal{O}(\vec{r}_k^N) = \frac{1}{L} \sum_{k=1}^L \mathcal{O}_k$$

sum over MC steps

(or every a certain amount of MC steps). Hence consider the following observable:

$$\bar{g}(\vec{r}; \vec{r}_1, \dots, \vec{r}_N) \equiv \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r}' - \vec{r}_{ij}) d\vec{r}'$$

i.e. $g(\vec{r})$ of one configuration (no average over $e^{-\beta U_N}/Z$).

Its average value is

$$\begin{aligned}
\langle \bar{g} \rangle &= \left\langle \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r}' - \vec{r}_{ij}) d\vec{r}' \right\rangle \\
&= \int \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r}' - \vec{r}_{ij}) d\vec{r}' \frac{e^{-\beta U_N}}{Z} d\vec{r}_1 \cdots d\vec{r}_N \\
&= \frac{1}{L} \sum_{k=1}^L \underbrace{\frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r}' - \vec{r}_{ij}^{(k)}) d\vec{r}'}_{\bar{g}_k} = \frac{1}{L} \sum_k \bar{g}_k.
\end{aligned}$$

$\bar{g}_k$ is our observable (as $\mathcal{O}_k$) calculated at the k -th MC step:

$$\bar{g}_k(\vec{r}) = \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N\rho} \sum'_{i,j} \delta(\vec{r}' - \vec{r}_{ij}^{(k)}) d\vec{r}' = \frac{1}{\Delta V \rho} \overbrace{\frac{1}{N} \sum_i}^{\text{average over all particles}} \underbrace{\int_{\Delta V_{\vec{r}}} \sum'_j \delta(\vec{r}' - \vec{r}_{ij}^{(k)}) d\vec{r}'}_{\substack{\# \text{ particles in } \Delta V_{\vec{r}} \text{ at a distance} \\ \vec{r} \text{ from particle } i}}.$$

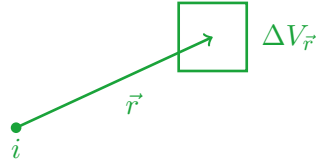


Figure 6.2: Small volume $\Delta V_{\vec{r}}$ at a distance $\vec{r}$ from particle i .

Box centred at i , of volume V , divided into M small boxes of volume ΔV :

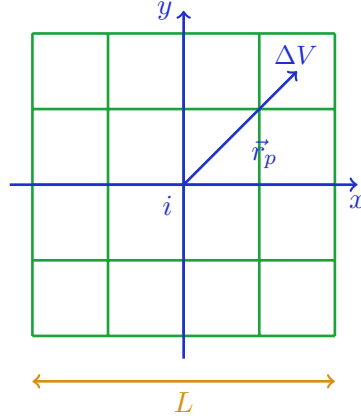


Figure 6.3: Cubic box of side L centred at particle i , divided into M small boxes of volume ΔV .

$\vec{r}_p$, with $p = 1, \dots, M$, is the centre of the p -th box of volume ΔV :

$$\vec{r}_p = \Delta r (k\hat{x} + \ell\hat{y} + m\hat{z}), \quad k, \ell, m \text{ integers},$$

thus obtaining

$$\bar{g}_k(\vec{r}_p) \simeq g_k(\vec{r}_p) \quad \text{if } \Delta V \text{ is small enough.}$$

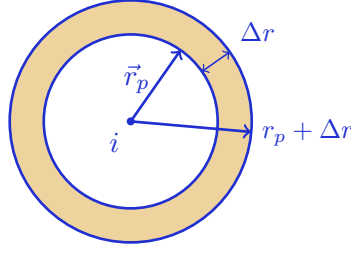


Figure 6.4: Spherical shell of radius r_p and thickness Δr around particle i .

6.1.5 Isotropic case

Spherical shell of thickness Δr :

$$\Delta V_p = 4\pi r_p^2 \Delta r.$$

$$\underbrace{\bar{g}_k(r_p)}_{\substack{\text{note that this} \\ \text{is a scalar}}} = \frac{1}{\underbrace{4\pi r_p^2 \Delta r \rho}_{\substack{\text{average number of} \\ \text{particles inside } \Delta V_p}}} \frac{1}{N} \sum_i^N \overbrace{\int_{\Delta V_p} \sum_j' \delta(\vec{r} - \vec{r}_{ij}) d\vec{r}}^{\substack{\# \text{ particles inside the } p\text{-th shell}}}.$$

$\bar{g}_k(r_p) \simeq g_k(r_p)$ if Δr is small enough is the radial distribution function.

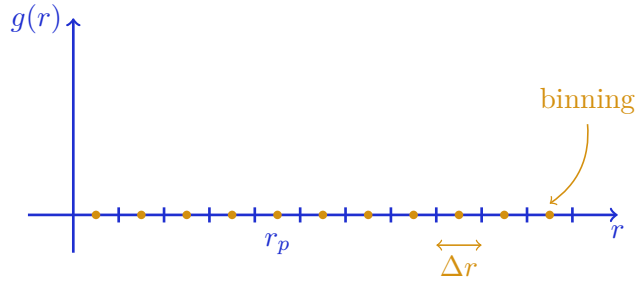


Figure 6.5: Binning of the r axis in intervals of width Δr ; r_p is the centre of the p -th bin.

Low concentrations. See Fig. 6.6.

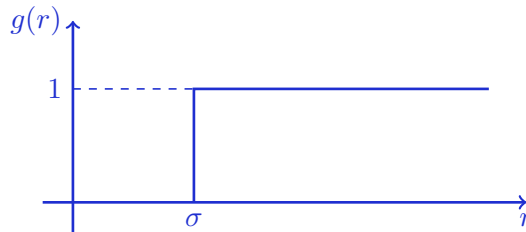


Figure 6.6: Radial distribution function at low concentrations.

High concentration in fluid phase. See Fig. 6.7.

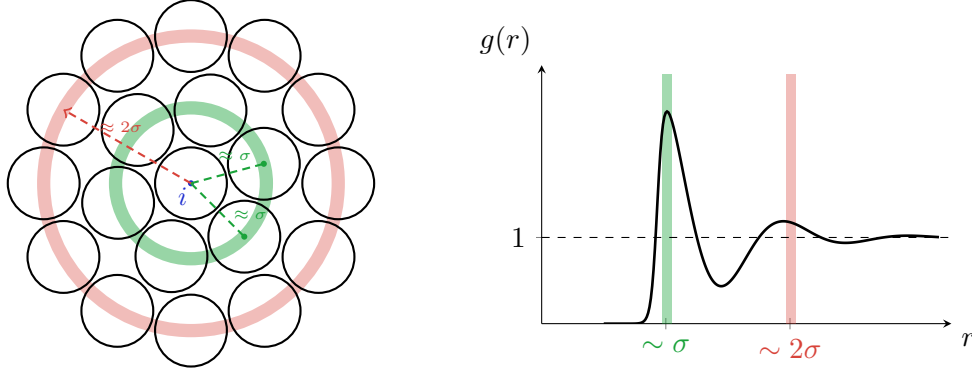


Figure 6.7: Dense fluid: the first shell of neighbours of particle i is at distance $\approx \sigma$ (green), the second one at $\approx 2\sigma$ (red); correspondingly $g(r)$ has peaks at $r \approx \sigma$ and $r \approx 2\sigma$.

6.2 Calculation of energy from $g(r)$

$$\begin{aligned}
 \langle U_N \rangle &= U_{\text{ex}} = \int \frac{1}{2} \sum'_{i,j} U_2(\vec{r}_{ij}) \frac{e^{-\beta U_N}}{Z} d^N \vec{r} \\
 &= \frac{1}{2} N(N-1) \int U_2(\vec{r}_{12}) \frac{e^{-\beta U_N}}{Z} d\vec{r}_1 d\vec{r}_2 d^{(N-2)} \vec{r} \\
 &= \frac{1}{2} \int U_2(\vec{r}_{12}) \underbrace{\int N(N-1) \frac{e^{-\beta U_N}}{Z} d^{(N-2)} \vec{r} d\vec{r}_1 d\vec{r}_2}_{\rho^{(2)}(\vec{r}_1, \vec{r}_2)} \\
 &= \frac{1}{2} \int U_2(\vec{r}_{12}) \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2.
 \end{aligned}$$

But

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^2 g(\vec{r}_{12}) \quad \leftarrow \text{homogeneous case,}$$

so that

$$U_{\text{ex}} = \frac{\rho^2}{2} \int U_2(\vec{r}_{12}) g(\vec{r}_{12}) d\vec{r}_1 d\vec{r}_2.$$

If we change variables $(\vec{r}_1, \vec{r}_2) \rightarrow (\vec{r}_2, \vec{r})$, where $\vec{r} = \vec{r}_{12} = \vec{r}_1 - \vec{r}_2$,

$$\begin{aligned}
 U_{\text{ex}} &= \frac{\rho^2}{2} \int U_2(\vec{r}) g(\vec{r}) d\vec{r} d\vec{r}_2 \\
 &= V \frac{\rho^2}{2} \int U_2(\vec{r}) g(\vec{r}) d\vec{r} = \langle U_N \rangle.
 \end{aligned}$$

If the system is isotropic

$$U_{\text{ex}} = V \frac{\rho^2}{2} \int U_2(r) \underbrace{g(r)}_{\text{radial distribution function}} 4\pi r^2 dr.$$

6.3 Tail corrections

In a simulation $U_{LJ}(r) \rightarrow U_{LJ}^c(r)$, where

$$U_{LJ}^c(r) = \begin{cases} U_{LJ}(r) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Hence

$$\begin{aligned}
U_{\text{ex}} = \langle U_N \rangle &= \frac{1}{2} V \rho^2 \int_0^\infty g(r) U_2(r) 4\pi r^2 dr \\
&= \overbrace{\frac{1}{2} V \rho^2 \int_0^{r_c} g(r) U_2(r) 4\pi r^2 dr}^{U_{\text{ex}}^c} + \underbrace{\frac{1}{2} V \rho^2 \int_{r_c}^\infty g(r) U_2(r) 4\pi r^2 dr}_{\text{tail correction}}.
\end{aligned}$$

U_{ex}^c : this is what we have from simulations, i.e. $\frac{1}{2} \sum'_{i,j} U_2^c(r_{ij})$.

Question: can we somehow estimate the tail correction?

$$\underbrace{U_{\text{ex}}^{\text{tail}}}_{\text{tail correction}} = \frac{1}{2} V \rho^2 \int_{r_c}^\infty g(r) U_2(r) 4\pi r^2 dr.$$

If r_c is large enough, for $r \geq r_c$ $g(r) \simeq 1$, hence

$$U_{\text{ex}}^{\text{tail}} = \frac{1}{2} V \rho^2 \int_{r_c}^\infty U_2(r) 4\pi r^2 dr \quad \leftarrow \text{this integral can be calculated.}$$

Example: Lennard-Jones system.

$$U_2(r) = U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

so that

$$U_{\text{ex}}^{\text{tail}} = \frac{1}{2} V \rho^2 \int_{r_c}^\infty 4\pi r^2 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] dr = V \frac{8\pi}{3} \epsilon \rho^2 \sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c} \right)^9 - \left(\frac{\sigma}{r_c} \right)^3 \right].$$

We can also do better:

$$\begin{aligned}
U_{\text{ex}} &= \overbrace{\frac{1}{2} V \rho^2 \int_0^{r_c} g(r) U_2(r) 4\pi r^2 dr}^{\text{energy from simulation}} \\
&\quad + \underbrace{\frac{1}{2} V \rho^2 \int_{r_c}^{L/2} g(r) U_2(r) 4\pi r^2 dr + \frac{1}{2} V \rho^2 \int_{L/2}^{+\infty} \overbrace{g(r)}^{\simeq 1} U_2(r) 4\pi r^2 dr}_{\text{tail correction}} \\
&= U_{\text{ex}}^c + U_{\text{ex}}^{\text{tail}},
\end{aligned}$$

where

$$U_{\text{ex}}^{\text{tail}} = \frac{1}{2} V \rho^2 \int_{r_c}^{L/2} \underbrace{g(r)}_{\substack{\text{calculated from} \\ \text{simulations}}} U_2(r) 4\pi r^2 dr + \frac{1}{2} V \rho^2 \int_{L/2}^{+\infty} U_2(r) 4\pi r^2 dr.$$

6.4 Calculation of pressure from $g(r)$

With $\mathcal{H} = K + U$:

$$P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V}, \quad F = -k_B T \ln Z,$$

but

$$Q = \frac{\Lambda^{-3N}}{N!} Z, \quad \text{where } \Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad \leftarrow \text{it does not depend on } V.$$

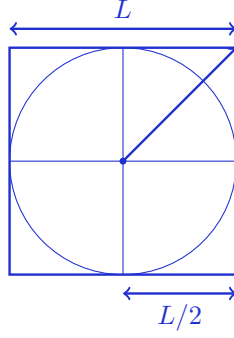


Figure 6.8: Box of side L : from a particle in the centre, all distances $r \leq L/2$ are sampled in every direction, while beyond $L/2$ (e.g. towards the corners) only part of the spherical shell lies in the box.

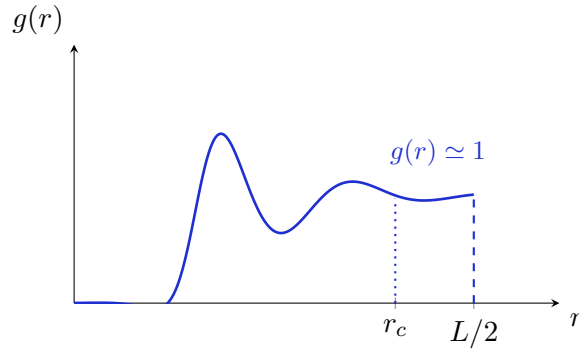


Figure 6.9: $g(r)$ from a simulation: between r_c and $L/2$ it is known from the simulation; beyond $L/2$ one assumes $g(r) \simeq 1$.

Moreover

$$Z = Z_{\text{id}} \cdot Z_{\text{ex}}, \quad Z_{\text{id}} = V^N, \quad Z_{\text{ex}} = \int e^{-\beta U_N(\vec{r}_1, \dots, \vec{r}_N)} d^N \vec{\xi},$$

with **scaled coordinates**:

$$\vec{r}_i = V^{1/3} \vec{\xi}_i.$$

Then

$$\begin{aligned} P &= k_B T \frac{\partial}{\partial V} (\ln Z_{\text{id}} + \ln Z_{\text{ex}}) = k_B T \frac{\partial \ln V^N}{\partial V} + k_B T \frac{\partial \ln Z_{\text{ex}}}{\partial V} \\ &= \underbrace{k_B T \rho}_{P_{\text{id}}} + \underbrace{k_B T \frac{\partial \ln Z_{\text{ex}}}{\partial V}}_{P_{\text{ex}}}, \\ &\quad P = P_{\text{id}} + P_{\text{ex}}, \\ P_{\text{ex}} &= k_B T \frac{1}{Z_{\text{ex}}} \frac{\partial Z_{\text{ex}}}{\partial V} = \frac{k_B T}{Z_{\text{ex}}} \frac{\partial}{\partial V} \left(\int_0^1 e^{-\beta U_N} d^N \vec{\xi} \right) = \dots \quad U_N = U_N(V^{1/3} \vec{\xi}_1, \dots, V^{1/3} \vec{\xi}_N) \\ &= -k_B T \int \frac{\partial U_N}{\partial V} \frac{e^{-\beta U_N} V^N}{\underbrace{Z_{\text{EX}} V^N}_Z} d^N \vec{\xi} = - \int \frac{\partial U_N}{\partial V} \frac{e^{-\beta U_N}}{Z} d^N \vec{r} = - \left\langle \frac{\partial U_N}{\partial V} \right\rangle. \end{aligned}$$

(*) Note that we can bring $\partial/\partial V$ inside the integral since the integration domain does not depend on V if we use scaled coordinates.

$$P = P_{\text{ID}} - \overbrace{\left\langle \frac{\partial U_N}{\partial V} \right\rangle}^{P_{\text{EX}}}.$$

With

$$U_N = \frac{1}{2} \sum'_{i,j} v_2(\vec{r}_{ij}), \quad V = L^3 \implies \frac{\partial}{\partial V} = \frac{1}{3L^2} \frac{\partial}{\partial L},$$

we have

$$\begin{aligned} P_{\text{EX}} &= - \left\langle \frac{1}{3L^2} \frac{\partial U_N}{\partial L} \right\rangle = - \left\langle \frac{1}{3L^2} \frac{\partial}{\partial L} \left(\frac{1}{2} \sum'_{i,j} v_2(\vec{r}_{ij}) \right) \right\rangle \\ &= - \left\langle \frac{1}{6L^2} \sum'_{i,j} \underbrace{\frac{\partial v_2}{\partial \vec{r}_{ij}}}_{-\vec{f}_{ij}} \cdot \frac{\partial \vec{r}_{ij}}{\partial L} \right\rangle = \left\langle \frac{1}{6L^3} \sum'_{i,j} \vec{f}_{ij} \cdot \vec{r}_{ij} \right\rangle, \quad \vec{\xi}_{ij} = \frac{\vec{r}_{ij}}{L}. \end{aligned}$$

Note that for a system with PBC we can restrict the calculation to the “first” box, so that

$$U_N = \frac{1}{2} \sum_{\vec{n}} \sum'_{i,j} v_2(\vec{r}_i - \vec{r}_j + L\vec{n})$$

where $\vec{n} = (n_x, n_y, n_z)$ with n_α integers. Hence

$$\begin{aligned} \frac{\partial U_N}{\partial L} &= \frac{1}{2} \sum'_{i,j} \frac{\partial v_2(\vec{r}_i - (\vec{r}_j + L\vec{n}))}{\partial L} = \frac{1}{2} \sum'_{i,j} \frac{\partial v_2}{\partial \vec{r}_{ij}} \cdot \frac{\partial (\vec{r}_i - (\vec{r}_j + L\vec{n}))}{\partial L}, \\ \text{but } \frac{\partial (\vec{r}_i - (\vec{r}_j + L\vec{n}))}{\partial L} &= \frac{\vec{r}_i - (\vec{r}_j + L\vec{n})}{L} = \frac{\vec{r}_{ij}}{L} \end{aligned}$$

where j runs also over periodic particles.

Therefore

$$P_{\text{EX}} = \frac{1}{6V} \left\langle \sum'_{i,j} \vec{f}_{ij} \cdot \vec{r}_{ij} \right\rangle \quad (\vec{f}_{ij}: \text{force acting between } i \text{ and } j)$$

and

$$P = \rho k_B T + \overbrace{\frac{1}{6V} \left\langle \sum'_{i,j} \vec{f}_{ij} \cdot \vec{r}_{ij} \right\rangle}^{P_{\text{EX}}}$$

[similar expression for the molecular pressure]

We can now write P_{EX} in terms of $g(\vec{r})$. All terms of $\sum'_{i,j}$ are equal, hence

$$P_{\text{EX}} = \frac{N(N-1)}{6V} \int \frac{e^{-\beta U_N}}{Z} \vec{f}_{12} \cdot \vec{r}_{12} d\vec{r}_1 d\vec{r}_2 d^{(N-2)}\vec{r} = \frac{1}{6V} \int \rho^{(2)}(\vec{r}_1, \vec{r}_2) \vec{f}_{12} \cdot \vec{r}_{12} d\vec{r}_1 d\vec{r}_2.$$

Change of variables: $(\vec{r}_1, \vec{r}_2) \rightarrow (\vec{r}, \vec{r}_2)$ where $\vec{r} = \vec{r}_1 - \vec{r}_2$:

$$P_{\text{EX}} = \frac{1}{6V} \int \rho^{(2)}(\vec{r} + \vec{r}_2, \vec{r}_2) \vec{f}(\vec{r}) \cdot \vec{r} d\vec{r} d\vec{r}_2.$$

If the system is homogeneous, $\rho^{(2)}(\vec{r} + \vec{r}_2, \vec{r}_2) = \rho^{(2)}(\vec{r})$, hence

$$P_{\text{EX}} = \frac{1}{6} \int \rho^{(2)}(\vec{r}) \vec{f}(\vec{r}) \cdot \vec{r} d\vec{r}.$$

But $\rho^{(2)}(\vec{r}) = \rho^2 g(\vec{r})$, so that

$$P_{\text{EX}} = \frac{\rho^2}{6} \int \vec{f}(\vec{r}) \cdot \vec{r} g(\vec{r}) d\vec{r}.$$

If the system is isotropic

$$P_{\text{EX}} = \frac{\rho^2}{6} \int_0^\infty f(r) g(r) 4\pi r^3 dr.$$

6.4.1 Tail corrections

$$P_{\text{EX}} = \overbrace{\frac{\rho^2}{6} \int_0^{r_c} f(r) g(r) 4\pi r^3 dr}^{P_{\text{SIM from simulations}}} + \underbrace{\frac{\rho^2}{6} \int_{r_c}^{+\infty} f(r) g(r) 4\pi r^3 dr}_{= P_{\text{TAIL}}} \quad .$$

for LJ we can calculate this analytically

(•) Note that

$$P_{\text{SIM}} = \frac{\rho^2}{6} \int_0^{r_c} f(r) g(r) 4\pi r^3 dr = \overbrace{\frac{1}{6V} \left\langle \sum'_{ij} \vec{f}_{ij}^c \cdot \vec{r}_{ij} \right\rangle}^{\text{we can calculate this from simulations}} .$$

The above tail correction applies if we want to compare our results with a system without cutoff, i.e. we have:

$$P = P_{\text{SIM}} + P_{\text{TAIL}}$$

Question: but what is the pressure of a system with truncated interactions?

For example consider a truncated LJ system (Fig. 6.10).

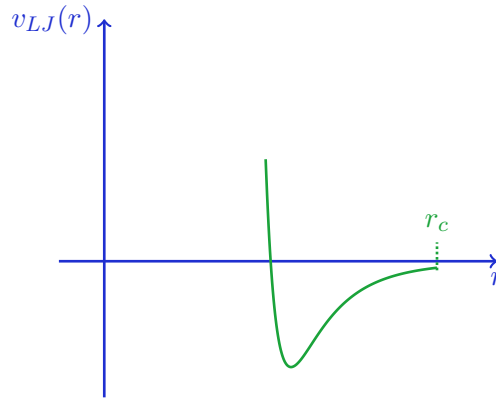


Figure 6.10: Lennard-Jones potential truncated at r_c .

Around r_c one has

$$v_{LJ}(r) \approx \theta(r_c - r) v_{LJ}(r_c) \quad \text{where} \quad \theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases}$$

$$f(r) = -\frac{dv_2}{dr} = v_{LJ}(r_c) \delta(r - r_c) \quad \text{since} \quad \frac{d}{dx} \theta(x) = \delta(x).$$

Hence we have

$$\begin{aligned} P_{\text{IMP}} &= \frac{1}{6} \rho^2 \int_{r_c-\epsilon}^{\infty} v_{LJ}(r_c) \delta(r - r_c) g(r) 4\pi r^3 dr = \frac{1}{6} \rho^2 v_{LJ}(r_c) g(r_c) 4\pi r_c^3 \\ &\simeq \frac{1}{6} \rho^2 v_{LJ}(r_c) 4\pi r_c^3 \end{aligned}$$

— “impulsive” correction to pressure.

6.5 Static structure factor

One-point density:

$$\rho(\vec{r}) = \left\langle \sum_i \delta(\vec{r} - \vec{r}_i) \right\rangle,$$

then

$$\langle \rho(\vec{k}) \rangle = \overbrace{\int \rho(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d\vec{r}}^{\text{Fourier transform}} = \left\langle \overbrace{\sum_i e^{-i\vec{k} \cdot \vec{r}_i}}^{\rho(\vec{k})} \right\rangle \quad (\langle \cdot \rangle: \text{ensemble average})$$

where

$$\rho(\vec{k}) = \sum_i e^{-i\vec{k} \cdot \vec{r}_i}.$$

We define

$$S(\vec{k}) \equiv \frac{1}{N} \langle \rho(\vec{k}) \rho^*(\vec{k}) \rangle$$

$[S(\vec{k}) \text{ can be measured experimentally through scattering experiments}]$

But

$$\begin{aligned} S(\vec{k}) &= \frac{1}{N} \left\langle \sum_{i,j} e^{-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle = 1 + \frac{1}{N} \left\langle \sum'_{i,j} e^{-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle \\ &= 1 + \frac{1}{N} \left\langle \int \sum'_{i,j} e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) d\vec{r} d\vec{r}' \right\rangle \\ &= 1 + \frac{1}{N} \int d\vec{r} d\vec{r}' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \overbrace{\left\langle \sum'_{i,j} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle}^{\rho^{(2)}(\vec{r}, \vec{r}')} \\ &= 1 + \frac{1}{N} \int d\vec{r} d\vec{r}' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \underbrace{\rho^{(2)}(\vec{r}, \vec{r}')}_{= \rho^2 g^{(2)}(\vec{r}, \vec{r}')} . \end{aligned}$$

Assuming the system homogeneous

$$S(\vec{k}) = 1 + \frac{\rho^2}{N} V \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} g(\vec{r}) = 1 + \rho \underbrace{\int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} g(\vec{r})}_{\text{Fourier transform of } g(\vec{r})} .$$

In the isotropic case $S(\vec{k}) = S(k)$, see Fig. 6.11.

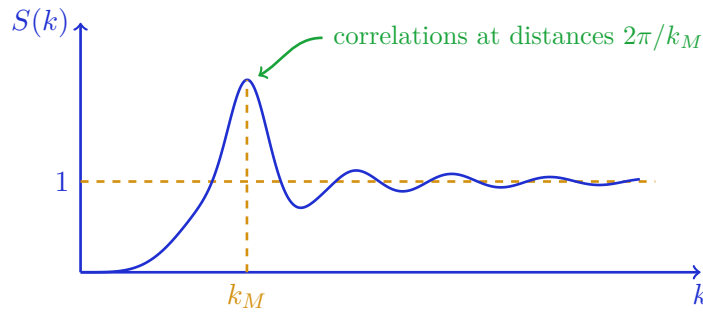


Figure 6.11: Static structure factor of a liquid in the isotropic case.

6.6 Mean squared displacement

$$\Delta r^2(t) = \frac{1}{N} \sum_{i=1}^N \|\vec{r}_i(t) - \vec{r}_i(0)\|^2$$

(Δr^2 is a function of t , the MC step; $\vec{r}_i(0)$ are the initial positions).

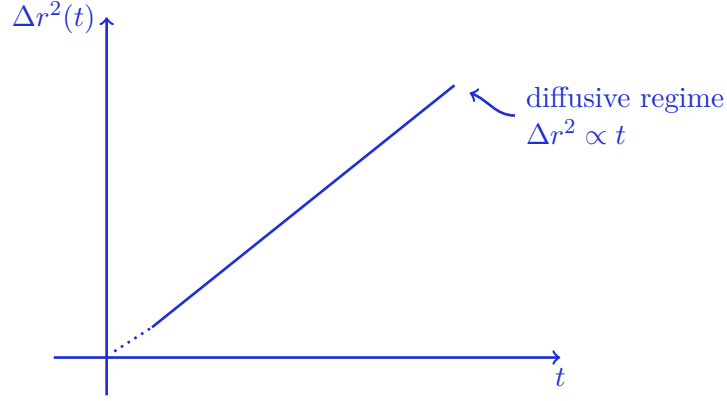


Figure 6.12: Mean squared displacement as a function of the number of MC steps.

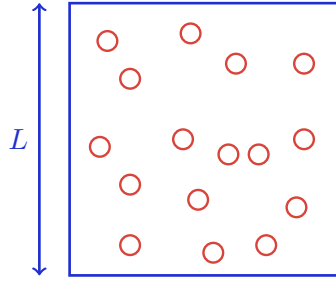


Figure 6.13: Particles in the simulation box of side L .

If

$$\sqrt{\Delta r^2} \gtrsim L$$

the system can be considered equilibrated, since all particles have moved enough, i.e. have fully explored the configuration space.

We could also use a less stringent condition, i.e.

$$\sqrt{\Delta r^2} \gtrsim \sigma \quad (\sigma: \text{typical particle size}).$$

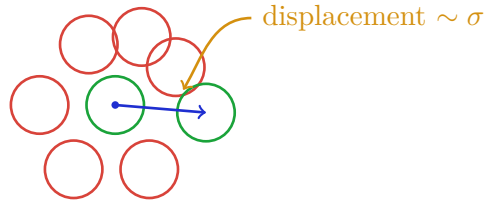


Figure 6.14: A particle displaced by about its own size among its neighbours.

The main contribution to spatial correlations comes from the first peak of $S(k)$, which roughly corresponds to a distance equal to σ .

Chapter 7

The isothermal–isobaric (NPT) ensemble

7.1 Metropolis Monte Carlo in the NPT ensemble

If ρ is a generic distribution

$$\rho(o) \cdot \pi(o \rightarrow n) = \rho(n) \pi(n \rightarrow o),$$

where

$$\pi(o \rightarrow n) = \overbrace{\alpha(o \rightarrow n)}^{\text{trial move}} \text{acc}(o \rightarrow n),$$

with

$$\text{acc}(o \rightarrow n) = \begin{cases} \rho(n)/\rho(o) & \text{if } \rho(n) \leq \rho(o) \\ 1 & \text{otherwise.} \end{cases}$$

Goal: find ρ for the NPT ensemble.

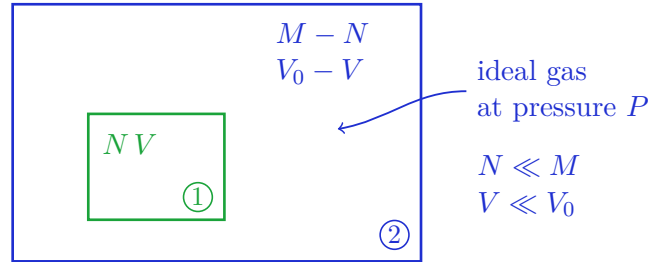


Figure 7.1: System (1) (N particles in the volume V) inside a much larger ideal gas (2) ($M - N$ particles in the volume $V_0 - V$) at pressure P .

Weakly interacting systems:

$$E_{\text{TOT}} = E_1 + E_2.$$

If the volumes of (1) and (2) are fixed

$$Q = \underbrace{\int \frac{d^{M-N} q}{\Lambda^{3(M-N)} (M-N)!}}_{(2)} \underbrace{\int \frac{dq^N e^{-\beta U_N}}{\Lambda^{3N} N!}}_{(1)}, \quad U_N = \frac{1}{2} \sum'_{ij} U_2(\vec{r}_{ij}),$$

where

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad \leftarrow \text{thermal wavelength.}$$

Let $V' = V_0 - V$; with *scaled coordinates*

$$\begin{aligned}\vec{q}_i &= V^{1/3} \vec{\xi}_i & \text{for } i \in \textcircled{1}, \\ \vec{q}_i &= (V')^{1/3} \vec{\xi}_i & \text{for } i \in \textcircled{2},\end{aligned}$$

we have

$$\begin{aligned}Q &= \frac{(V')^{M-N} V^N}{\Lambda^{3M} (M-N)! N!} \underbrace{\int d^{M-N} \xi}_{=1} \int d^{3N} \xi e^{-\beta U_N} \\ &= \frac{(V')^{M-N} V^N}{\Lambda^{3M} (M-N)! N!} \int d^N \xi e^{-\beta U_N}.\end{aligned}$$

If the volume is allowed to change

$$Q = \underbrace{\int dV}_{\text{we have also to sum over all possible volumes}} \frac{(V')^{M-N} V^N}{\Lambda^{3M} (M-N)! N!} \int d^N \xi e^{-\beta U_N}.$$

For the NVT ensemble

$$Z = \int e^{-\beta U_N} d^N q, \quad \rho \propto e^{-\beta U_N},$$

hence we have

$$\rho(\underbrace{V, \vec{\xi}_1, \dots, \vec{\xi}_N}_{\text{state of the system}}) \propto e^{-\beta U_N} V^N \overbrace{(V_0 - V)^{M-N}}^{V'}.$$

Note that to implement a Metropolis MC we need ρ only up to a constant, since the acceptance probability depends on $\rho(n)/\rho(o)$.

Consider the term

$$(V_0 - V)^{M-N} = V_0^{M-N} \left(1 - \frac{V}{V_0}\right)^{M-N} = V_0^{M-N} \left(1 - \rho \frac{V}{M-N}\right)^{M-N} = \dots$$

If $M \gg N$, i.e. $M - N \rightarrow +\infty$,

$$\lim_{M-N \rightarrow +\infty} \left(1 - \frac{\rho V}{M-N}\right)^{M-N} = e^{-\rho V} \quad \left(\lim_{x \rightarrow +\infty} \left(1 + \frac{k}{x}\right)^x = e^k\right),$$

so that

$$\dots = V_0^{M-N} e^{\overbrace{-\rho V}^{= -\beta P V}} = V_0^{M-N} e^{-\beta P V}, \quad \beta P = \rho \quad (\text{heat bath}).$$

Hence:

$$\rho(V, \vec{\xi}_1, \dots, \vec{\xi}_N) \propto e^{\overbrace{N \ln V}^{V^N}} e^{-\beta P V} e^{-\beta U_N}.$$

The state of the system is given by $\{V, \vec{\xi}_1, \dots, \vec{\xi}_N\}$, hence we need to update both V and $\{\vec{\xi}_1, \dots, \vec{\xi}_N\}$, i.e. we need two types of trial moves: a **particle move** (updating randomly a particle) and a **volume move**.

7.1.1 1) Particle move

Choose randomly a particle and update its position $\vec{\xi}_i$.

Now note that if we update the position of particle i as in a NVT MC, i.e.

$$\vec{r}'_i = \vec{r}_i + \Delta\vec{r},$$

this is equivalent to do

$$V^{1/3} \vec{\xi}'_i = V^{1/3} \vec{\xi}_i + \Delta\vec{r}, \quad \text{i.e.} \quad \vec{\xi}'_i = \vec{\xi}_i + V^{-1/3} \Delta\vec{r},$$

i.e. we are updating $\vec{\xi}_i$ as requested. Then accept this trial move as follows:

$$\begin{aligned} \text{acc}(o \rightarrow n) &= \min \left\{ 1, \frac{e^{N \ln V'} e^{-\beta P V'} e^{-\beta U_N(V, \vec{\xi}_1, \dots, \vec{\xi}'_i, \dots, \vec{\xi}_N)}}{e^{N \ln V} e^{-\beta P V} e^{-\beta U_N(V, \vec{\xi}_1, \dots, \vec{\xi}_N)}} \right\} \\ &= \min \{ 1, e^{-\beta \Delta U_N} \}. \end{aligned}$$

Note that this move is equivalent to that of a NVT MC.

7.1.2 2) Volume move

$$\left. \begin{aligned} \vec{r}_i &= V^{1/3} \vec{\xi}_i, & \vec{r}'_i &= (V')^{1/3} \vec{\xi}_i \\ & & \vec{r}'_i &= \vec{r}_i \left(\frac{V'}{V} \right)^{1/3} \end{aligned} \right\} \text{volume move}$$

$$V' = V + \delta V \eta, \quad \eta \in (-1, 1) \quad \leftarrow \text{random},$$

and

$$\begin{aligned} \text{acc}(o \rightarrow n) &= \min \left\{ 1, \frac{\rho(V', \vec{\xi}_1, \dots, \vec{\xi}_N)}{\rho(V, \vec{\xi}_1, \dots, \vec{\xi}_N)} \right\} \\ &\quad \underbrace{\hspace{1.5cm}}_{= \rho(n)/\rho(o)} \\ &= \min \left\{ 1, \frac{e^{-\beta U_N(V') - \beta P V' + N \ln V'}}{e^{-\beta U_N(V) - \beta P V + N \ln V}} \right\}. \end{aligned}$$

If

$$G \equiv U_N + P V - k_B T N \ln V,$$

$$\Delta G = P \Delta V + \Delta U_N - N k_B T \ln \left(\frac{V(n)}{V(o)} \right), \quad \Delta V = V' - V, \quad \Delta U_N = U_N(V') - U_N(V).$$

Acceptance probability NPT:

$$\text{acc}(o \rightarrow n) = \min \{ 1, e^{-\beta \Delta G} \}.$$

Note that:

- 1) δV must be optimized to have an acceptance rate of volume moves around 30%–50% (as δ);
- 2) the two types of move are selected randomly, where the probability of selecting a volume move should be equal to $1/N$ (because each box move involves N particles);
- 3) MC NPT: the volume performs a random walk (fluctuates), see Fig. 7.2.

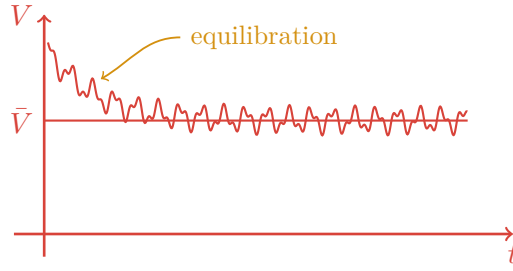


Figure 7.2: NPT MC: after the equilibration the volume fluctuates around its average value $\bar{V}$.

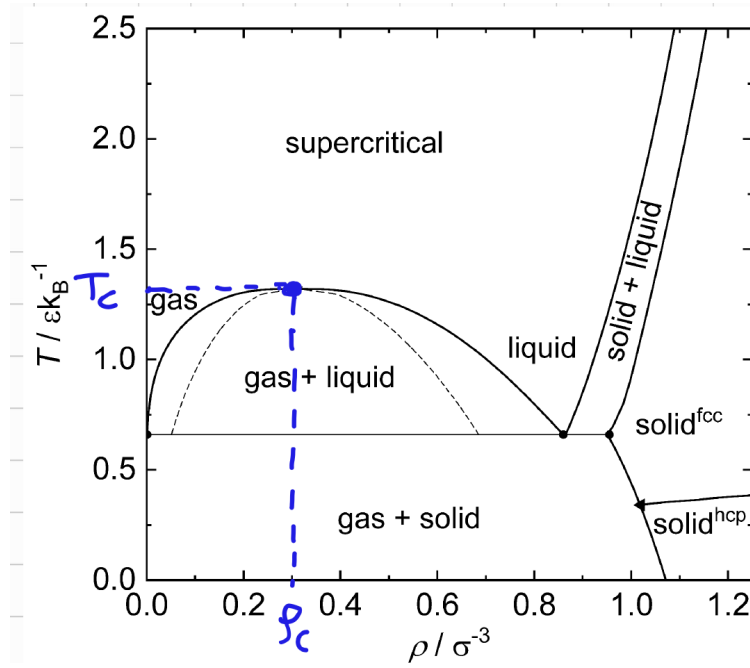


Figure 7.3: Phase diagram of the Lennard-Jones system in the (ρ, T) plane, with the critical point (ρ_c, T_c) marked. Source: S. Stephan et al., as reproduced in Wikipedia, “Lennard-Jones potential”.

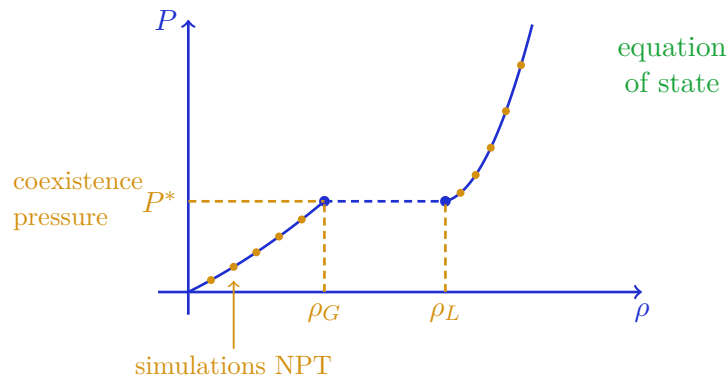


Figure 7.4: Equation of state $P(\rho)$ for $T < T_c$ obtained from NPT simulations (dots): the two branches end at ρ_G and ρ_L , which coexist at the pressure P^* .

7.2 Lennard-Jones phase diagram

See Fig. 7.3.

For $T < T_c$ (Fig. 7.4):

Probability of a given configuration:

$$\rho(V, \vec{\xi}_1, \dots, \vec{\xi}_N) = \frac{e^{-\beta U_N} e^{-\beta PV} V^N}{\int e^{-\beta U_N} e^{-\beta PV} V^N dV d^N \vec{\xi}}.$$

Probability of the volume V :

$$\begin{aligned} \rho(V) &= \int \frac{e^{-\beta U_N} e^{-\beta PV} V^N}{\int e^{-\beta U_N} e^{-\beta PV} V^N dV d^N \vec{\xi}} d^N \vec{\xi} \\ &= \frac{1}{Z_{\text{NPT}}} e^{-\beta PV} \overbrace{\int e^{-\beta U_N} V^N d^N \vec{\xi}}^{Z(T,V)} = \frac{e^{-\beta PV} Z(T, V)}{Z_{\text{NPT}}}, \end{aligned}$$

where

$$Z(T, V) = \int e^{-\beta U_N} V^N d^N \vec{\xi} \quad \text{and} \quad Z_{\text{NPT}} = \int e^{-\beta U_N} e^{-\beta PV} V^N dV d^N \vec{\xi}.$$

7.2.1 Gibbs free energy

$$Q_{\text{NPT}} \equiv \frac{Z_{\text{NPT}}}{\Lambda^{3N} N!} \quad \leftarrow \text{we also consider the integral over momenta and the correct Boltzmann counting},$$

$$-k_B T \ln(Q_{\text{NPT}}) = -k_B T \ln \left(\int e^{-\beta U_N} e^{-\beta PV} V^N \frac{dV d^N \vec{\xi}}{\Lambda^{3N} N!} \right).$$

The contribution to the integral will come mostly from $\bar{V} = \langle V \rangle$, hence we can write:

$$\begin{aligned} -k_B T \ln(Q_{\text{NPT}}) &\simeq -k_B T \ln \left(\int e^{-\beta U_N} e^{-\beta P \bar{V}} \bar{V}^N \frac{d^N \vec{\xi}}{\Lambda^{3N} N!} \right) \\ &= -k_B T \ln \left(e^{-\beta P \bar{V}} \int e^{-\beta U_N} \bar{V}^N \frac{d^N \vec{\xi}}{\Lambda^{3N} N!} \right). \end{aligned}$$

But

$$\int e^{-\beta U_N} \bar{V}^N \frac{d^N \vec{\xi}}{\Lambda^{3N} N!} = \underbrace{Q_N(T, \bar{V})}_{\text{canonical partition function}},$$

hence

$$\begin{aligned} -k_B T \ln(Q_{\text{NPT}}) &= P \bar{V} - k_B T \ln Q_N(T, \bar{V}) = P \bar{V} + F(T, \bar{V}) \\ &= G(T, P) \quad \leftarrow \text{Gibbs free energy}. \end{aligned}$$

$$G(V) \equiv -k_B T \ln \rho(V) + K \quad \leftarrow K: \text{constant which is independent of } V.$$

One phase. See Fig. 7.5.

Two-phase coexistence (phases I and II).

$$P = P^* = \{\text{coexistence pressure}\}.$$

$$\begin{aligned} F(V) &= G(V) - PV \\ &\quad \uparrow \\ &\quad \text{intended as } \bar{V} = \langle V \rangle \\ \frac{\partial F}{\partial V} \Big|_{V=V_I} &= -P^*, \quad \underbrace{\frac{\partial F}{\partial V} \Big|_{V=V_{\text{II}}}}_{\text{common tangent}} = -P^*. \end{aligned}$$

In general $P \neq P^*$, hence we cannot be exactly at coexistence, i.e. (Fig. 7.8)

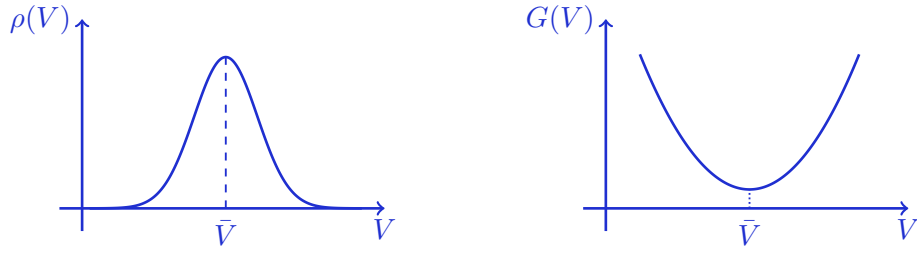


Figure 7.5: One phase: $\rho(V)$ has a single peak at $\bar{V}$ and $G(V)$ a single minimum.

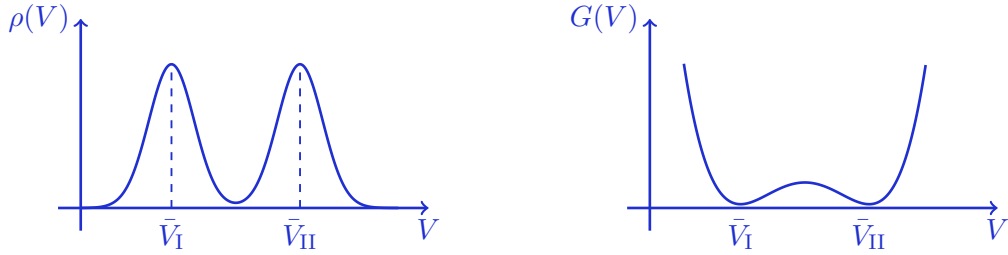


Figure 7.6: Two-phase coexistence: $\rho(V)$ has two peaks of equal height at $\bar{V}_I$ and $\bar{V}_{II}$, and $G(V)$ two equal minima.

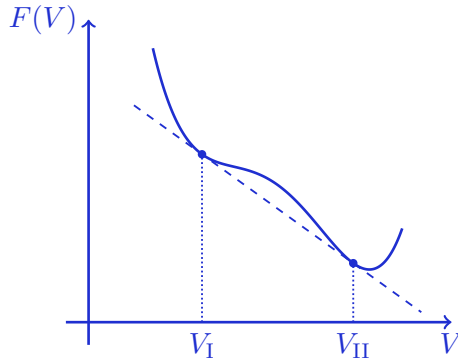


Figure 7.7: Common-tangent construction on $F(V)$: the tangent touches F at V_I and V_{II} and has slope $-P^*$.

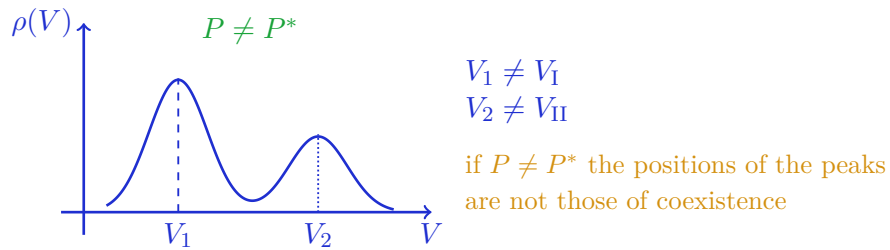


Figure 7.8: Off coexistence ($P \neq P^*$) the two peaks of $\rho(V)$ have different heights and are not located at the coexistence volumes.

7.2.2 Histogram reweighting

$$\begin{aligned}
 \rho(V, P_1) &= \frac{e^{-\beta P_1 V} Z(T, V)}{Z_{\text{NPT}}(T, P_1)} && \leftarrow \text{from a simulation at } P = P_1 \neq P^* \\
 \rho(V, P_2) &= \frac{e^{-\beta P_2 V} Z(T, V)}{Z_{\text{NPT}}(T, P_2)} \\
 \frac{\rho(V, P_2)}{\rho(V, P_1)} &= \frac{e^{-\beta P_2 V} \cancel{Z(T, V)}}{e^{-\beta P_1 V} \cancel{Z(T, V)}} \frac{Z_{\text{NPT}}(T, P_1)}{Z_{\text{NPT}}(T, P_2)}, \\
 \rho(V, P_2) &= \rho(V, P_1) \cdot e^{-\beta(P_2 - P_1)V} k
 \end{aligned} \tag{1}$$

where

$$k = \frac{Z_{\text{NPT}}(T, P_1)}{Z_{\text{NPT}}(T, P_2)} \quad \leftarrow \text{which is independent of } V \text{ (normalization).}$$

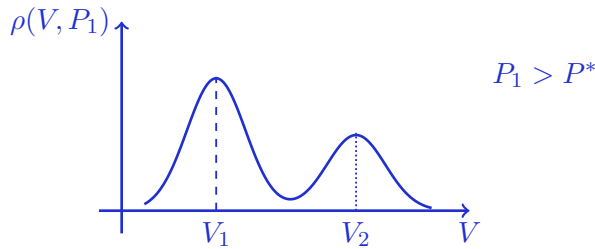


Figure 7.9: Volume histogram from a simulation at $P_1 > P^*$.

By using Eq. (1) we can search for P_2 such that the two following areas (orange and green hatched) are equal, i.e. the two phases are equally likely ($\leftarrow$ histogram reweighting), see Fig. 7.10.

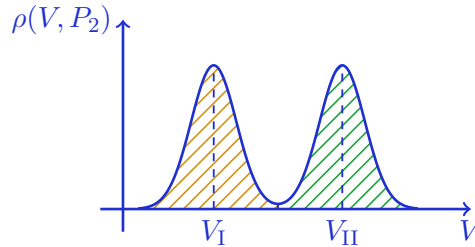


Figure 7.10: Volume histogram reweighted to the pressure P_2 at which the two areas are equal.

$$\rho_I = \frac{N}{V_I}, \quad \rho_{II} = \frac{N}{V_{II}}.$$

If we are not at coexistence we can employ histogram reweighting; anyway we have to be close enough ($P_1 \approx P^*$) so that $\rho(V_{II}, P_1)$ is not negligible (within simulation times).

SHOW `histogram_reweighting.nb` (Mathematica)

7.3 Changes of the box shape (Parrinello–Rahman)

Allow for changes of the box shape.

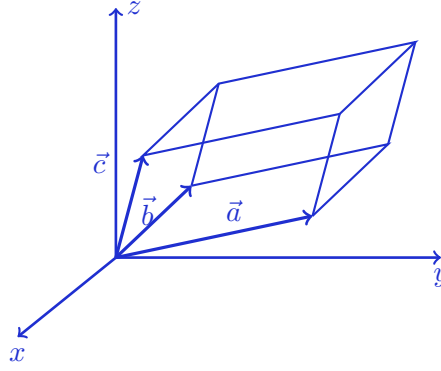


Figure 7.11: Simulation box with non-orthogonal edges $\vec{a}$, $\vec{b}$, $\vec{c}$.

$$\left. \begin{aligned} \vec{a} &= (a_x, a_y, a_z) \\ \vec{b} &= (b_x, b_y, b_z) \\ \vec{c} &= (c_x, c_y, c_z) \end{aligned} \right\} \text{edges of the simulation box (not orthogonal)}$$

$$Q = \underbrace{\frac{(V_0 - V)^{M-N}}{\Lambda^{3(M-N)} (M-N)!}}_{\text{heat bath}} \underbrace{\int \frac{e^{-\beta U_N}}{\Lambda^{3N} N!} d^N \vec{r}}_{\text{our system with non-orthogonal edges}}$$

Reduced coordinates:

$$\vec{r}_i = \underbrace{\begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}}_{\mathbf{M}} \vec{\xi}_i.$$

Note that if

$$\mathbf{M} = \begin{pmatrix} L & 0 & 0 \\ 0 & L & 0 \\ 0 & 0 & L \end{pmatrix}$$

we have the standard NPT ensemble.

$$Q = \frac{(V_0 - V)^{M-N}}{\Lambda^{3(M-N)} (M-N)!} \int \frac{e^{-\beta U_N}}{\Lambda^{3N} N!} |\det \mathbf{M}|^N d^N \xi.$$

But:

7.3.1 Box volume

This formula for the volume can be understood from the above figure. The volume of the parallelepiped is the area of the base times the height. From the geometric definition of the cross product, we know that its magnitude, $\|\mathbf{a} \times \mathbf{b}\|$, is the area of the parallelogram base, and that the direction of the vector $\mathbf{a} \times \mathbf{b}$ is perpendicular to the base. The height of the parallelepiped is the component of $\mathbf{c}$ in the direction normal to the base, i.e., in the direction of $\mathbf{a} \times \mathbf{b}$. Hence the height is $\|\mathbf{c}\| |\cos \phi|$, where ϕ is the angle between $\mathbf{c}$ and $\mathbf{a} \times \mathbf{b}$. (Why do we need the absolute value? If we swapped the locations of $\mathbf{a}$ and $\mathbf{b}$, in the above figure, then $\mathbf{a} \times \mathbf{b}$ would point downward. The angle ϕ would be larger than $\pi/2$, and $\cos \phi$ would be negative.)

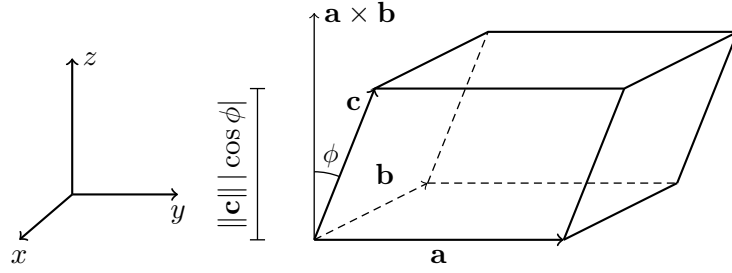


Figure 7.12: Volume of the parallelepiped spanned by the three vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ (redrawn from Math Insight, “The formula for the volume of a parallelepiped”).

$$V = |\vec{c} \cdot (\vec{a} \times \vec{b})| = \det \underbrace{\begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}}_{\mathbf{M}} = \det \mathbf{M},$$

so that

$$\rho(V, \vec{\xi}_1, \dots, \vec{\xi}_N) \propto e^{-\beta U_N} e^{-\beta P V} V^N$$

and

$$\text{acc}(o \rightarrow n) = \min\left\{1, \frac{\rho(V', \vec{\xi}'_1, \dots, \vec{\xi}'_N)}{\rho(V, \vec{\xi}_1, \dots, \vec{\xi}_N)}\right\} = \min\{1, e^{-\beta \Delta G}\},$$

with

$$G = U + P V - k_B T N \ln V.$$

In general

$$\mathbf{M} = \begin{pmatrix} a_x & b_x & c_x \\ 0 & b_y & c_y \\ 0 & 0 & c_z \end{pmatrix} \quad \leftarrow \text{by doing \#1 and \#2 (Fig. 7.13) we can reduce to this matrix.}$$

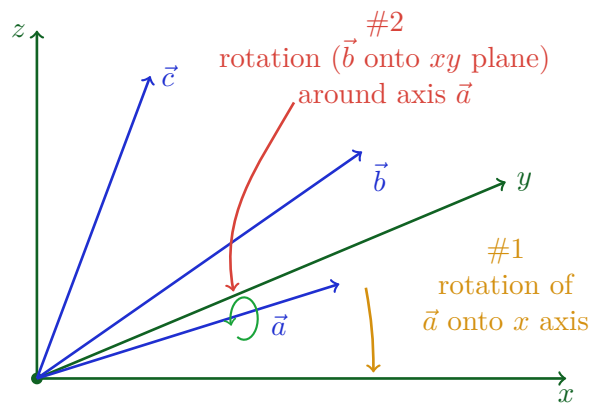


Figure 7.13: Reduction of $\mathbf{M}$ to upper-triangular form: #1 rotate $\vec{a}$ onto the x axis; #2 rotate around $\vec{a}$ to bring $\vec{b}$ onto the xy plane.

xyz is the lab frame.

7.3.2 Special cases

1)

$$M = \begin{pmatrix} \gamma L_x & 0 & 0 \\ 0 & \gamma L_y & 0 \\ 0 & 0 & \gamma L_z \end{pmatrix} \quad \begin{array}{l} \text{anisotropic box (i.e. not cubic)} \\ \text{but isotropic volume moves.} \end{array}$$

In this case γ changes randomly in a volume move, i.e.

$$\gamma' = \gamma + \Delta\gamma, \quad \Delta\gamma = \Delta\gamma_0 \eta,$$

where $\eta \in [-1, 1]$ is a stochastic variable.

2)

$$M = \begin{pmatrix} L_x & 0 & 0 \\ 0 & L_y & 0 \\ 0 & 0 & L_z \end{pmatrix} \quad \begin{array}{l} \text{anisotropic box where the 3 edge sizes} \\ \text{can change independently.} \end{array}$$

In a volume move a direction α is selected randomly and

$$L'_\alpha = L_\alpha + \Delta L, \quad \alpha \in \{x, y, z\},$$

and

$$\Delta L = \Delta L_0 \underset{\text{random}}{\eta}, \quad \eta \in [-1, 1].$$

This type of move can be useful for crystals and liquid crystals (see below).

Example: smectic phase. See Fig. 7.14.

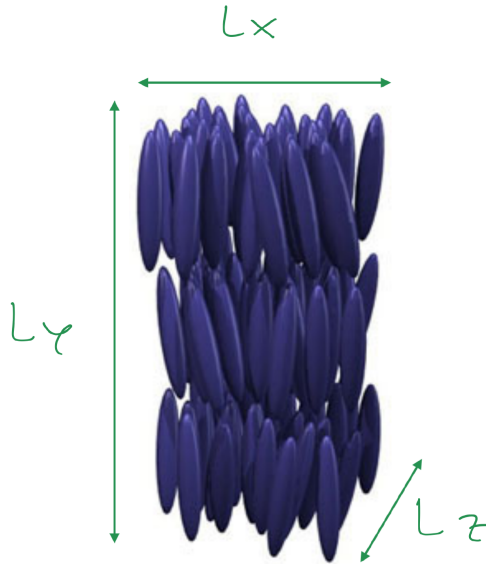


Figure 7.14: Smectic phase of elongated particles: the layered structure requires $L_y \neq L_x, L_z$.

$$L_y \neq L_x, L_z$$

Chapter 8

Orientalional moves

8.1 Uniaxial particles

Uniaxial particles (e.g. cylinders).

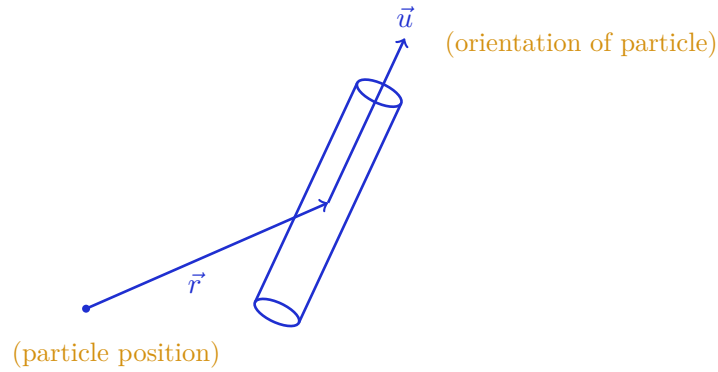


Figure 8.1: Uniaxial particle (cylinder): position $\vec{r}$ and orientation $\vec{u}$.

System state:

$$(\vec{r}_1, \vec{u}_1, \dots, \vec{r}_N, \vec{u}_N).$$

Choose randomly whether doing a translational or a rotational move. The translational move is like we already discussed.

Rotational trial move ($\alpha(o \rightarrow n)$).

$$\vec{u}_o \longrightarrow \vec{u}_n = \frac{\vec{u}_o + \gamma \Delta \vec{u}}{\|\vec{u}_o + \gamma \Delta \vec{u}\|},$$

where $\Delta \vec{u}$ is a random unit vector (Marsaglia algorithm).

γ must be optimized as δ . Acceptance does not change.

This move is symmetric, i.e.

$$\alpha(o \rightarrow n) = \alpha(n \rightarrow o).$$

$\alpha(o \rightarrow n)$

$$\|\Delta \vec{u}\| = \|\Delta \vec{u}'\| = 1.$$

$$\vec{u}_n = \frac{\vec{u}_o + \gamma \Delta \vec{u}}{\|\vec{u}_o + \gamma \Delta \vec{u}\|} = \frac{\vec{u}_o + \gamma \Delta \vec{u}'}{\|\vec{u}_o + \gamma \Delta \vec{u}'\|},$$

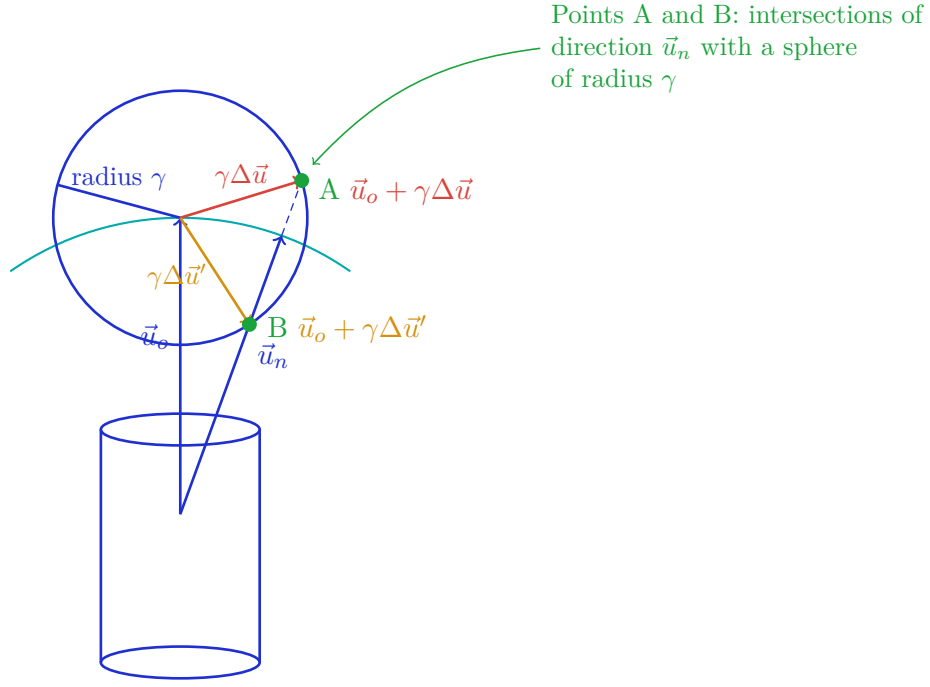


Figure 8.2: Forward move $\alpha(o \rightarrow n)$: the two points A and B, where the direction of $\vec{u}_n$ intersects the sphere of radius γ centred at the tip of $\vec{u}_o$, both generate the same $\vec{u}_n$. The green arc is the unit sphere.

i.e. $\Delta \vec{u}$ and $\Delta \vec{u}'$ give the same $\vec{u}_n$.

If you do the same construction from $\vec{u}_n$ you will have that the probability is the same (chance of generating two orientations on the unit sphere). Indeed:

$\alpha(n \rightarrow o)$

$$\|\Delta \vec{u}\| = \|\Delta \vec{u}'\| = 1.$$

$$\vec{u}_o = \frac{\vec{u}_n + \gamma \Delta \vec{u}}{\|\vec{u}_n + \gamma \Delta \vec{u}\|} = \frac{\vec{u}_n + \gamma \Delta \vec{u}'}{\|\vec{u}_n + \gamma \Delta \vec{u}'\|},$$

i.e. $\Delta \vec{u}$ and $\Delta \vec{u}'$ give the same $\vec{u}_o$.

Hence $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$, i.e. the probability is the same, being the chance of generating two orientations on the unit sphere.

8.2 Non-uniaxial particles

System state:

$$(\vec{r}_1, \Omega_1, \dots, \vec{r}_N, \Omega_N), \quad \text{e.g. } \Omega_i = (\theta_i, \psi_i, \phi_i) \quad \text{Euler angles.}$$

Alternative to Euler angles: rotation matrix R such that

$$\begin{array}{c} \vec{x}' \\ \uparrow \\ \text{body} \\ \text{reference} \\ \text{frame} \end{array} = R \left(\begin{array}{c} \vec{x} \\ \uparrow \\ \text{laboratory} \\ \text{frame} \end{array} - \vec{x}_0 \right).$$

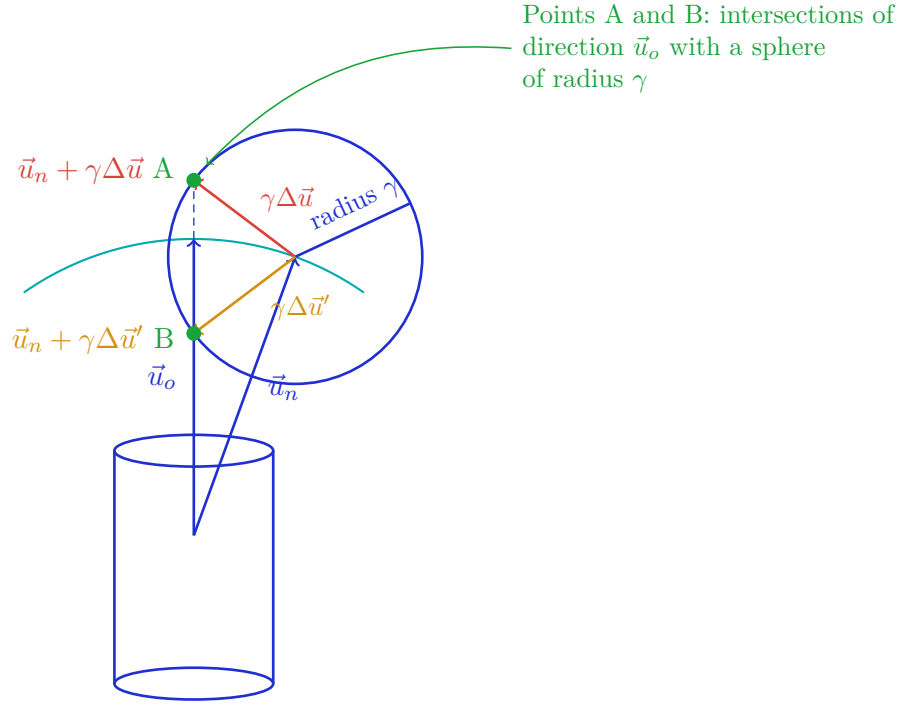


Figure 8.3: Reverse move $\alpha(n \rightarrow o)$: same construction starting from $\vec{u}_n$; A and B now lie on the direction of $\vec{u}_o$ and both generate $\vec{u}_o$.

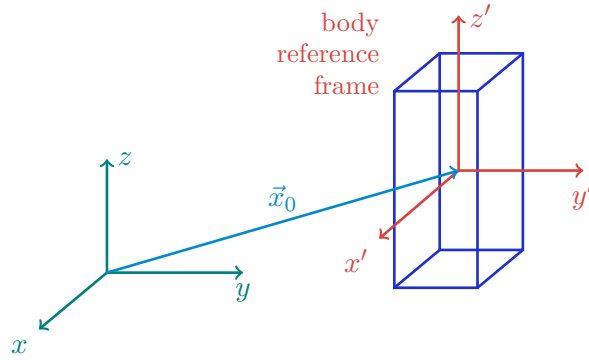


Figure 8.4: Non-uniaxial particle: laboratory frame and body reference frame centred at $\vec{x}_0$.

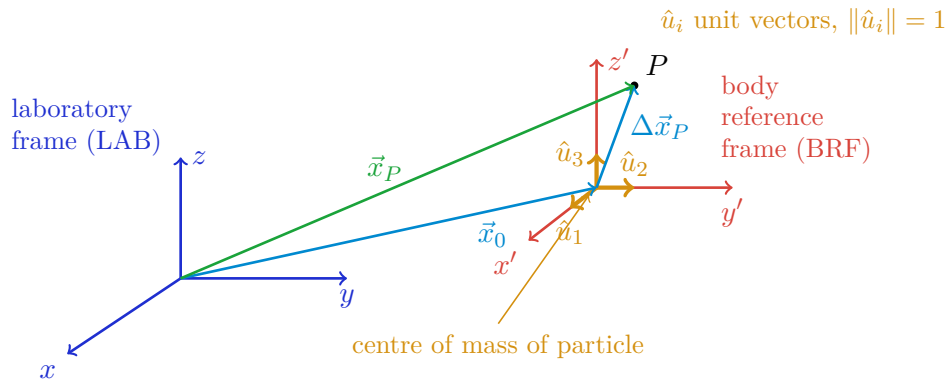


Figure 8.5: Laboratory frame (LAB) and body reference frame (BRF) of a particle with centre of mass $\vec{x}_0$; P is a point of the particle.

8.3 A closer look at the rotation matrix

$$\begin{aligned}\vec{x}_P &= (x, y, z) && \text{LAB} \\ \vec{x}'_P &= (x', y', z') && \text{BRF}\end{aligned}$$

vectors whose coordinates are expressed in lab frame

$$\vec{x}_P = \overbrace{\vec{x}_0 + (\vec{x}_P - \vec{x}_0)} = \vec{x}_0 + \Delta\vec{x}_P.$$

$$\Delta\vec{x}_P = x' \hat{u}_1 + y' \hat{u}_2 + z' \hat{u}_3 \quad (x', y', z': \text{BRF coordinates of } P),$$

i.e. (with $\hat{u}_1, \hat{u}_2, \hat{u}_3$ intended as column vectors)

$$\Delta\vec{x}_P = \begin{pmatrix} \boxed{u_{1x}} & \boxed{u_{2x}} & \boxed{u_{3x}} \\ \boxed{u_{1y}} & \boxed{u_{2y}} & \boxed{u_{3y}} \\ \boxed{u_{1z}} & \boxed{u_{2z}} & \boxed{u_{3z}} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \underbrace{\begin{pmatrix} \hat{u}_1 & \hat{u}_2 & \hat{u}_3 \end{pmatrix}}_{\text{column vectors}} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}.$$

If we define

$$R \equiv \begin{pmatrix} \boxed{u_{1x}} & \boxed{u_{1y}} & \boxed{u_{1z}} \\ \boxed{u_{2x}} & \boxed{u_{2y}} & \boxed{u_{2z}} \\ \boxed{u_{3x}} & \boxed{u_{3y}} & \boxed{u_{3z}} \end{pmatrix} \quad \leftarrow \text{each row is a unit vector},$$

then

$${}^tR = \begin{pmatrix} \boxed{u_{1x}} & \boxed{u_{2x}} & \boxed{u_{3x}} \\ \boxed{u_{1y}} & \boxed{u_{2y}} & \boxed{u_{3y}} \\ \boxed{u_{1z}} & \boxed{u_{2z}} & \boxed{u_{3z}} \end{pmatrix} \quad \text{transpose of } R,$$

so that

$$\Delta\vec{x}_P = {}^tR \vec{x}'_P.$$

Note that

$${}^tR R = \mathbb{I}, \quad \text{hence} \quad {}^tR = R^{-1}.$$

I.e.

$$\begin{aligned}\vec{x}_P &= \vec{x}_0 + \underset{\text{LAB}}{\Delta\vec{x}_P} = \vec{x}_0 + \underset{\text{BRF}}{{}^tR \vec{x}'_P}, \\ \vec{x}'_P &= R(\vec{x}_P - \vec{x}_0).\end{aligned}$$

Given a point in the body reference frame, its coordinates in the lab reference frame can be obtained through the rotation matrix.

Rotational trial move. If we rotate a particle by an angle $\Delta\theta$ around an axis $\hat{u}_R = (u_x \ u_y \ u_z)$ we have

$$R' = R \left(\underset{\substack{\text{a matrix defined in the following} \\ \downarrow \\ \text{identity matrix}}}{I} + M(\Delta\theta) \right) \quad (1)$$

where

$$M(\Delta\theta) = -\sin(\Delta\theta) \Omega + (1 - \cos(\Delta\theta)) \Omega^2$$

with

$$\Omega = \begin{pmatrix} 0 & -u_z & u_y \\ u_z & 0 & -u_x \\ -u_y & u_x & 0 \end{pmatrix} \quad u_x, u_y, u_z: \text{coordinates of the rotation axis in the lab frame.}$$

Hence a rotational trial move $\alpha(o \rightarrow n)$ of particle i is

$$\begin{array}{c} (\vec{r}_i, R_i) \\ \text{old } (o) \end{array} \longrightarrow \begin{array}{c} (\vec{r}_i, R'_i) \\ \text{new } (n) \end{array},$$

R_i is updated according to Eq. (1), where $\hat{u}_R$ is chosen randomly on the unit sphere and $\Delta\theta$ is random, i.e.

$$\Delta\theta = \Delta\theta_{\max} \xi_\theta \quad \text{with } \xi_\theta \in [-1, 1],$$

where $\Delta\theta_{\max}$ must be optimized in order to have an acceptance ratio for the rotational move around 30–50%.

Note that this move is symmetric ($\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$) since to go back we have to choose the same orientation $\hat{u}_R$ and a rotation angle $-\Delta\theta$.

This orientational move is symmetric:

$$\alpha(o \rightarrow n) = \alpha(n \rightarrow o).$$

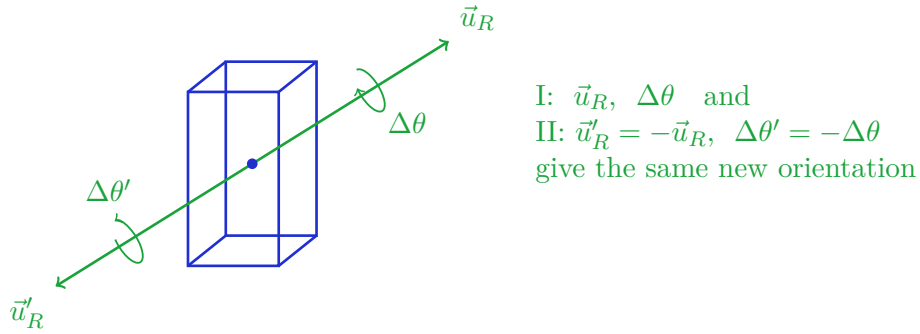


Figure 8.6: Forward move: the rotations I ($\vec{u}_R, \Delta\theta$) and II ($-\vec{u}_R, -\Delta\theta$) give the same new orientation.

$\alpha(o \rightarrow n)$ Remember that

$$R^n = R^o (I + M(\Delta\theta)) \quad \text{with} \quad M(\Delta\theta) = -\sin(\Delta\theta) \Omega + (1 - \cos(\Delta\theta)) \Omega^2.$$

If $\vec{u} \rightarrow -\vec{u}$ and $\Delta\theta \rightarrow -\Delta\theta$:

$$\begin{aligned} \sin(\Delta\theta) &\rightarrow -\sin(\Delta\theta), \\ \cos(\Delta\theta) &\rightarrow \cos(-\Delta\theta) = \cos(\Delta\theta), \\ \Omega &\rightarrow -\Omega, \end{aligned}$$

hence M is identical for rotations I and II.

$\alpha(n \rightarrow o)$ Hence

$$\alpha(o \rightarrow n) = \alpha(n \rightarrow o).$$

8.4 Random unit vectors

Spherical coordinates for generating a random unit vector lead to wrong results (if θ and ϕ are picked from uniform distributions).

$$d\Omega = \sin \theta d\theta d\phi.$$

See the Marsaglia algorithm for a correct way of generating random unit vectors.

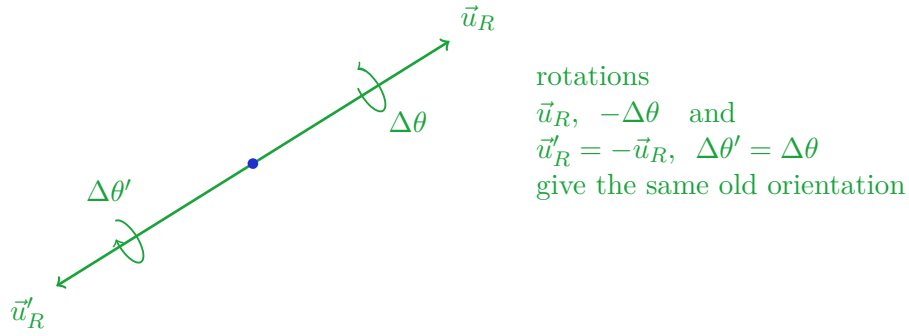


Figure 8.7: Reverse move: the rotations $(\vec{u}_R, -\Delta\theta)$ and $(-\vec{u}_R, \Delta\theta)$ give back the same old orientation.

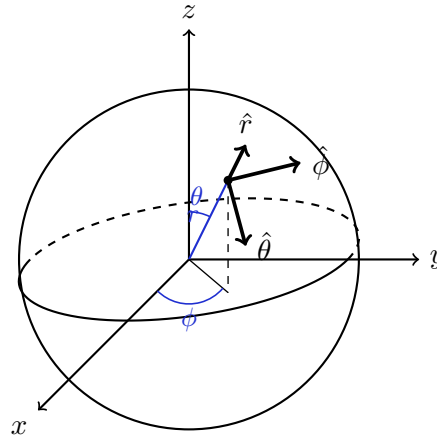
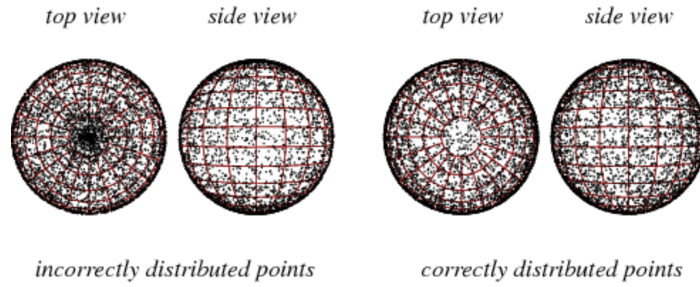


Figure 8.8: Spherical coordinates: θ is the polar angle, ϕ the azimuthal angle (redrawn from a pasted MathWorld figure, “Spherical Coordinates”, where the roles of θ and ϕ are exchanged).



To pick a random point on the surface of a **unit sphere**, it is incorrect to select **spherical coordinates** θ and ϕ from uniform distributions $\theta \in [0, 2\pi]$ and $\phi \in [0, \pi]$, since the area element $d\Omega = \sin\phi \, d\theta \, d\phi$ is a function of ϕ , and hence points picked in this way will be “bunched” near the poles (left figure above).

Figure 8.9: Sphere point picking: points generated with θ and ϕ uniformly distributed (left) have a **higher probability at the poles**; correctly distributed points (right). Source: Wolfram MathWorld, “Sphere Point Picking” (there ϕ denotes the polar angle).

8.5 Another possibility: quaternions

$$\vec{q} = (q_0, q_1, q_2, q_3), \quad \|\vec{q}\| = 1.$$

represents particle orientation

Indeed each can be mapped to a rotation matrix and vice versa.

$R \rightarrow \vec{q}$

$$\mathbf{q}_{\text{IB}} = \begin{bmatrix} \cos(\psi/2) \\ 0 \\ 0 \\ \sin(\psi/2) \end{bmatrix} \begin{bmatrix} \cos(\theta/2) \\ 0 \\ \sin(\theta/2) \\ 0 \end{bmatrix} \begin{bmatrix} \cos(\phi/2) \\ \sin(\phi/2) \\ 0 \\ 0 \end{bmatrix}$$

$$= \begin{bmatrix} \cos(\phi/2) \cos(\theta/2) \cos(\psi/2) + \sin(\phi/2) \sin(\theta/2) \sin(\psi/2) \\ \sin(\phi/2) \cos(\theta/2) \cos(\psi/2) - \cos(\phi/2) \sin(\theta/2) \sin(\psi/2) \\ \cos(\phi/2) \sin(\theta/2) \cos(\psi/2) + \sin(\phi/2) \cos(\theta/2) \sin(\psi/2) \\ \cos(\phi/2) \cos(\theta/2) \sin(\psi/2) - \sin(\phi/2) \sin(\theta/2) \cos(\psi/2) \end{bmatrix} \quad \phi, \theta, \psi: \text{ Euler angles}$$

Euler angles can be obtained from the rotation matrix.

$\vec{q} \rightarrow R$

$$R = \begin{bmatrix} 1 - 2(q_2^2 + q_3^2) & 2(q_1 q_2 - q_0 q_3) & 2(q_0 q_2 + q_1 q_3) \\ 2(q_1 q_2 + q_0 q_3) & 1 - 2(q_1^2 + q_3^2) & 2(q_2 q_3 - q_0 q_1) \\ 2(q_1 q_3 - q_0 q_2) & 2(q_0 q_1 + q_2 q_3) & 1 - 2(q_1^2 + q_2^2) \end{bmatrix}$$

State of the system:

$$(\vec{r}_1, \vec{q}_1, \dots, \vec{r}_N, \vec{q}_N), \quad \|\vec{q}_i\| = 1.$$

The rotational trial move $\alpha(o \rightarrow n)$ consists in doing:

$$\vec{q}_n = \frac{\vec{q}_o + \gamma \Delta \vec{q}}{\|\vec{q}_o + \gamma \Delta \vec{q}\|} \quad (\gamma \text{ must be optimized like } \delta \text{ for translations}),$$

where $\Delta \vec{q}$ is a random unit vector on the 4D unit sphere (again by using the Marsaglia algorithm), and

$$\gamma = \gamma_{\text{max}} \xi_\gamma, \quad \xi_\gamma \in [-1, 1],$$

and γ_{max} must be optimized to have a 30–50% acceptance rate of orientational moves.